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Collection Methods and Laboratory Processing of Samples from Donnelly Training Area Firing Points, Alaska, 2003

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ABSTRACT

At firing points for 105-mm howitzers, 2,4-DNT is detectable in the surface soils. 2,4-DNT is listed as a hazardous substance by the EPA and several states, including Alaska. Sample collection methods and laboratory subsampling procedures were developed to estimate the mean concentration of 2,4-DNT at a sparsely vegetated firing point. Collection of replicate 50-increment samples, where the <2-mm fraction was approximately 3 kg, was found to be adequate to estimate a statistically valid upper confidence limit of the mean concentration of 2,4-DNT from a 10,800-m^2 area. The 95% upper confidence limit was 0.7 μg/g for multi-increment samples collected by five different samplers. In contrast, collection of replicate 50-increment samples from heavily vegetated firing points did not provide normally distributed estimates of 2,4-DNT concentrations, indicating that more increments and more mass are needed per sample. Sample corers that yield uniform sampling depths of vegetated surfaces may also improve precision of the field samples. Accurate estimation of 2,4-DNT in the multi-increment samples required that the entire sample be extracted with solvent or the entire sample be subjected to grinding on a ring mill. Size fractionation studies revealed that most of the 2,4-DNT in the firing range soils was in the 0.595- to 2-mm size range, although the bulk of the soil was less than 0.595 mm prior to grinding. The 2,4-DNT appears to be in particulate form, most likely within fibers of the nitrocellulose-based propellant. Grinding for five minutes was needed to pulverize the propellant fibers sufficiently so that analytical subsamples could be obtained in a reproducible manner. We have adopted the practice of grinding firing point soils for five one-minute intervals, with time for heat dissipation between grinds, prior to obtaining replicate 10-g subsamples.

CONTENTS

ILLUSTRATIONS

TABLES

PREFACE

This report was prepared by Marianne E. Walsh, Chemical Engineer, Environmental Sciences Branch, Engineer Research and Development Center-Cold Regions Research and Engineering Laboratory (ERDC-CRREL), Hanover, New Hampshire; Charles A. Ramsey, EnviroStat, Fort Collins, Colorado; Charles M. Collins, Physical Scientist, Environmental Sciences Branch, ERDC-CRREL; Alan D. Hewitt, Research Physical Scientist, Environmental Sciences Branch, ERDC-CRREL; Michael R. Walsh, Mechanical Engineer, Engineering Resources Branch, ERDC-CRREL; Kevin L. Bjella, Physical Science Technician, Environmental Sciences Branch, ERDC-CRREL; Dennis J. Lambert, Engineering Resources Branch, ERDC-CRREL; and Nancy M. Perron, Snow and Ice Branch, ERDC-CRREL.

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1 INTRODUCTION

In 2001 and 2002 we sampled several 105-mm howitzer firing points at the Donnelly Training Area (DTA), Alaska, to determine the concentrations of 2,4-dinitrotoluene (2,4-DNT), a propellant residue (Walsh et. al. 2001, 2004). 2,4-DNT was easily detectable in most of the surface samples from each of the firing points, and concentrations were typically in the low parts-per-million range. However, estimates of 2,4-DNT concentrations from replicate multi-increment and discrete samples from the same location in the field showed that sampling error was large. We hypothesized that most of the 2,4-DNT was associated with fibers of the nitrocellulose-based propellant that was heterogeneously dispersed on the ground surface. These polymeric fibers also contributed to unacceptably high laboratory subsampling error, even in samples that had been sieved and ground on a ring mill for 60 s.

The state of Alaska has published soil cleanup levels for 2,4-DNT (Alaska Department of Environmental Conservation 2002). Therefore, statistically valid estimates of mean 2,4-DNT concentration in the soil must be obtained so that correct decisions can be made regarding the need for any potential remedial action.

Our objectives in 2003 were to develop sampling methods to determine mean concentrations of 2,4-DNT in the surface soil (top 2.5 cm) of a sparsely vegetated 105-mm firing point with specified statistical confidence that the mean is above or below the soil cleanup level. We also further explored the sampling problems associated with vegetated firing points, where the underlying mineral soil may be several centimeters below the ground surface (O horizon) on which we suspect that the propellant fibers reside. Lastly, we performed several experiments designed to understand and reduce laboratory subsampling error for firing point surface samples.

2 METHODS

Field sample collection methods

Field sample collection for estimates of mean 2,4-DNT concentrations in 100-m^2 and/or 10,000-m^2 areas of indirect fire firing points

FP Mark. FP Mark (Fig. 1 and 2) is a sparsely vegetated firing point where glacial till is covered with a veneer of loess. The border of the firing point with the surrounding forest is vegetated and the surface is covered with birch (*Betula nana*), aspen (*Populus tremuloides*), willow (*Salix planifolia*), blueberry (*Vaccinium uliginosum*), lingonberry (*Vaccinium vits-idaea*), bearberry (*Arctostaphylos uva-ursi*), lichens (*Stereocaulon*), and grasses (*Elymus trachycaulus*). The firing point is bisected by the road leading to Twin Lakes (Fig. 1). We chose to perform our sampling experiments to the north and east of the road where, in 2002, we collected 44 multi-increment samples surrounding an individual howitzer (Gun #2) one week and again five weeks after the howitzer was used in a firing exercise (Fig. 3) (Walsh et al. 2004). In 2002, each surface soil sample was nominally made up of 30 increments collected from random locations within a 2-m × 6-m area with an AMS #3 (American Falls, Idaho) scoop to a depth of 1 cm. The range of 2,4-DNT concentrations at FP Mark Gun #2 was <0.001 to 19 µg/g shortly after firing in June and 0.002 to 32 µg/g 30 days later in July. We did not detect a significant difference between the June and July concentration estimates of 2,4-DNT, nor did we detect gradients in concentration with distance from the howitzer. The concentration estimates that we obtained were not normally distributed, rendering the arithmetic mean a poor estimate for comparison to a cleanup level.

Discrete and multi-increment sampling from a 10-m × 10-m grid. For the first sampling experiment in 2003, our objective was to examine various sampling methods to estimate the 2,4-DNT concentration in a 10-m × 10-m area near the middle of the firing point. We re-established the sampling location from 2002 that was 50-m distance from the firing platform and 30 degrees to the right of the gun barrel. In 2002, our sampling methods estimated that the 2,4-DNT concentration in the surface soil (top 1 cm) in this location was 2.0 µg/g in June and 2.3 µg/g in July. FP Mark was used in August 2002, when 165 105-mm howitzer projectiles were fired. To confirm that 2,4-DNT was still present at this location, a multi-increment sample (443 g) was collected. The entire <2-mm fraction (266 g) was extracted with 300 mL of acetone. The acetone was filtered and analyzed on a field-portable gas chromatograph equipped with a thermionic detector (GC-TID) (Hewitt et al. 2001). The estimated 2,4-DNT concentration was 0.92 µg/g.

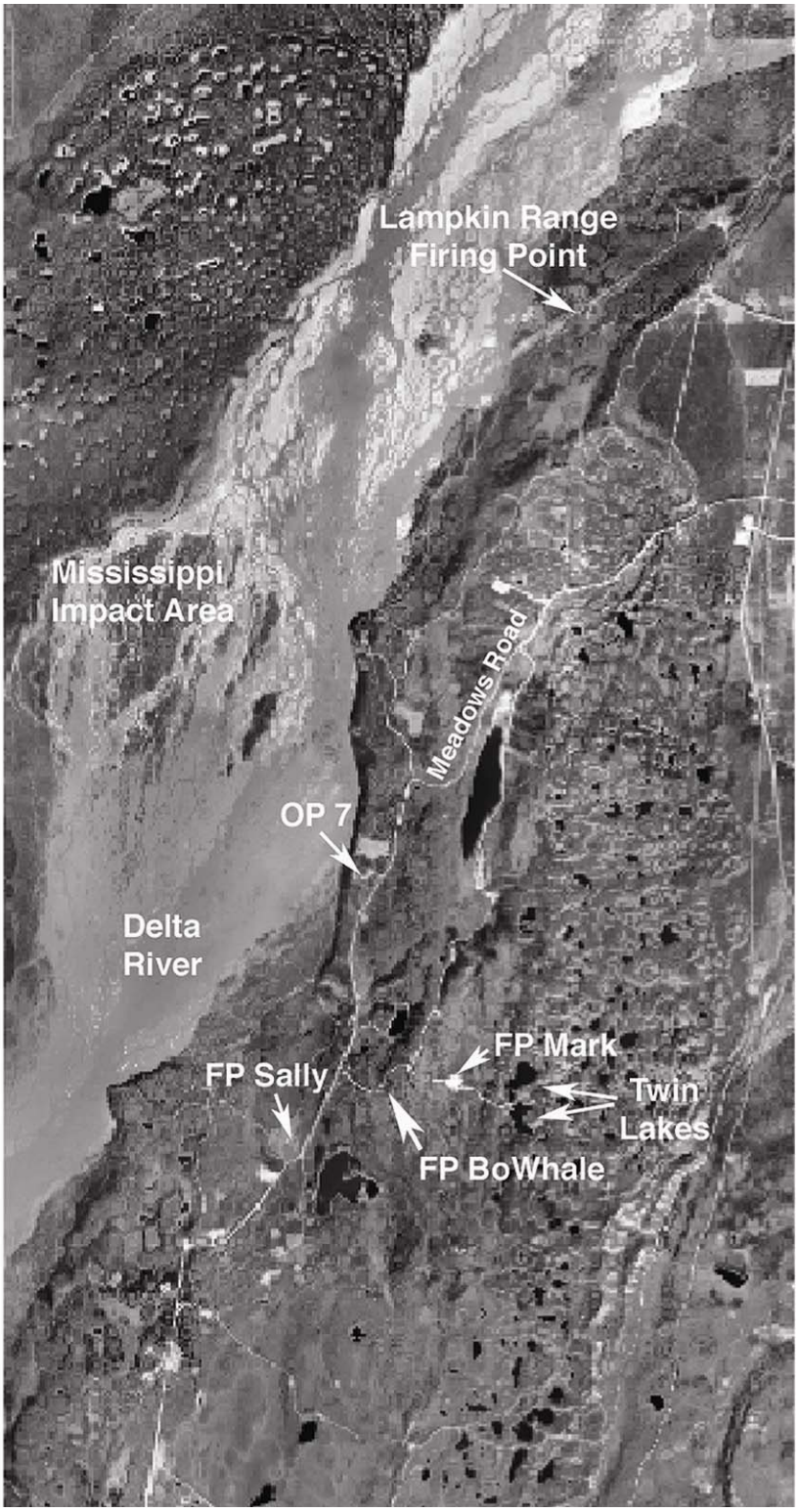

Figure 1. Orthophoto (AeroMap U.S. 2003) taken in August 2002 showing locations of DTA firing points.

Figure 2. Ground view of FP Mark.

Once we knew that the analyte of interest was still present at a sufficiently high concentration for our sampling experiments, we established a 10-m- × 10-m-square grid that was further divided into one hundred 1-m × 1-m cells (Fig. 4). Within each cell, we collected a discrete sample of the surface soil using an AMS #3 sampling scoop to a depth of 2.5 cm and placed the soil in 120-mL glass jars. To provide an estimate of short range heterogeneity, 20 cells were randomly chosen and a duplicate discrete sample was collected from each. Discrete samples were approximately 100 g each. Also within these 20 cells, a 10-increment sample of the surface soil was collected to obtain an estimate of the average 2,4-DNT concentration in each 1-m × 1-m cell. These 10-increment samples were approximately 1.5 kg each. Finally, to compare estimates of the mean 2,4-DNT concentration in the 10-m × 10-m grid determined by discrete sampling versus that obtained by multi-increment sampling, we collected ten 30-increment samples, which were approximately 4 kg each. The increments were taken from random locations within the 10-m × 10-m grid.

Multi-increment samples from 90-m × 120-m area (wide area). Our next series of experiments was designed to estimate the mean concentration of 2,4-DNT over a much larger area. The area north and east of the road bisecting FP Mark (Fig. 5) was approximately 100 times larger than the 10-m × 10-m grid. We collected four sets of samples to determine the variability introduced by the number of increments used to form a multi-increment sample and the variability introduced by each individual sampler's technique.

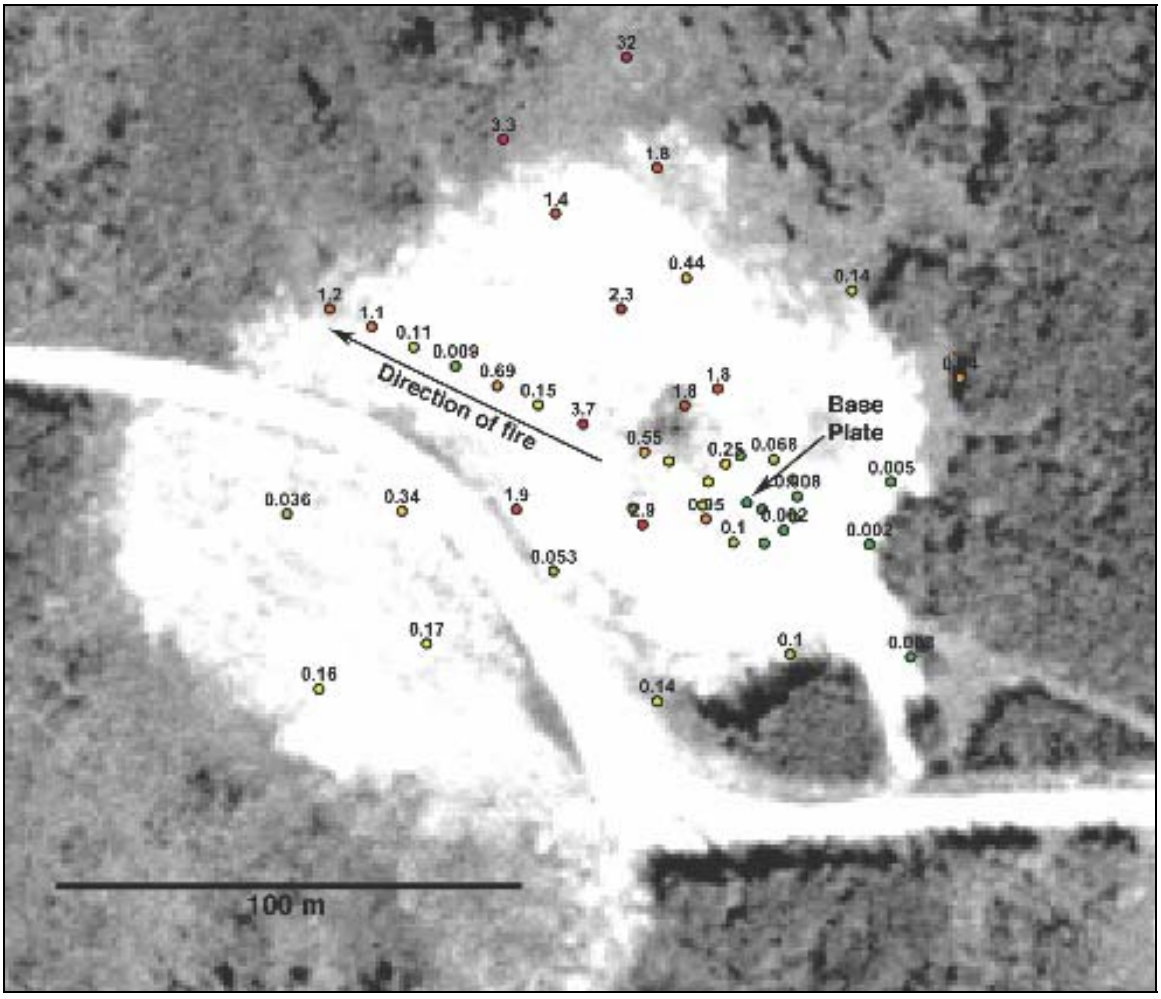

Figure 3. Locations and 2,4-DNT concentration (µg/g) around a 105-mm howitzer firing position at FP Mark in July 2002.

The desired sampling method was demonstrated to our six-member sampling team (i.e., insert AMS sampling scoop 2.5 cm into soil, twist to scribe a circle and loosen the soil, remove soil from scribed area). Five samplers each collected a 50-increment sample and a 200-increment sample. The multi-increment samples were collected so that the entire area was represented in the sample. Each sampler chose a corner of the area to be sampled and collected an increment of surface soil. Then the sampler walked to the adjacent corner of the area to be sampled and collected an increment of soil at a predetermined number of paces (15 paces for the 50-increment sample and 7.5 paces for the 200-increment sample). Once at the opposite corner, the sampler turned 90 degrees and walked

the predetermined number of paces and collected a sample, turned 90 degrees and again traversed the area, collecting increments and counting paces until the entire area was sampled (Fig. 5a). Meanwhile, the sixth sampler collected six replicate 50-increment samples and one 100-increment sample using the same sampling method. For the fourth series of samples, three samplers collected triplicate 50-increment samples using the random walk method (Fig. 5b). Again, the entire area was covered, but the sampler's path was meandering and the distance between subsamples was not regular.

Figure 4. Grid (10-m × 10-m) at FP Mark where discrete and multi-increment samples were collected in July 2003.

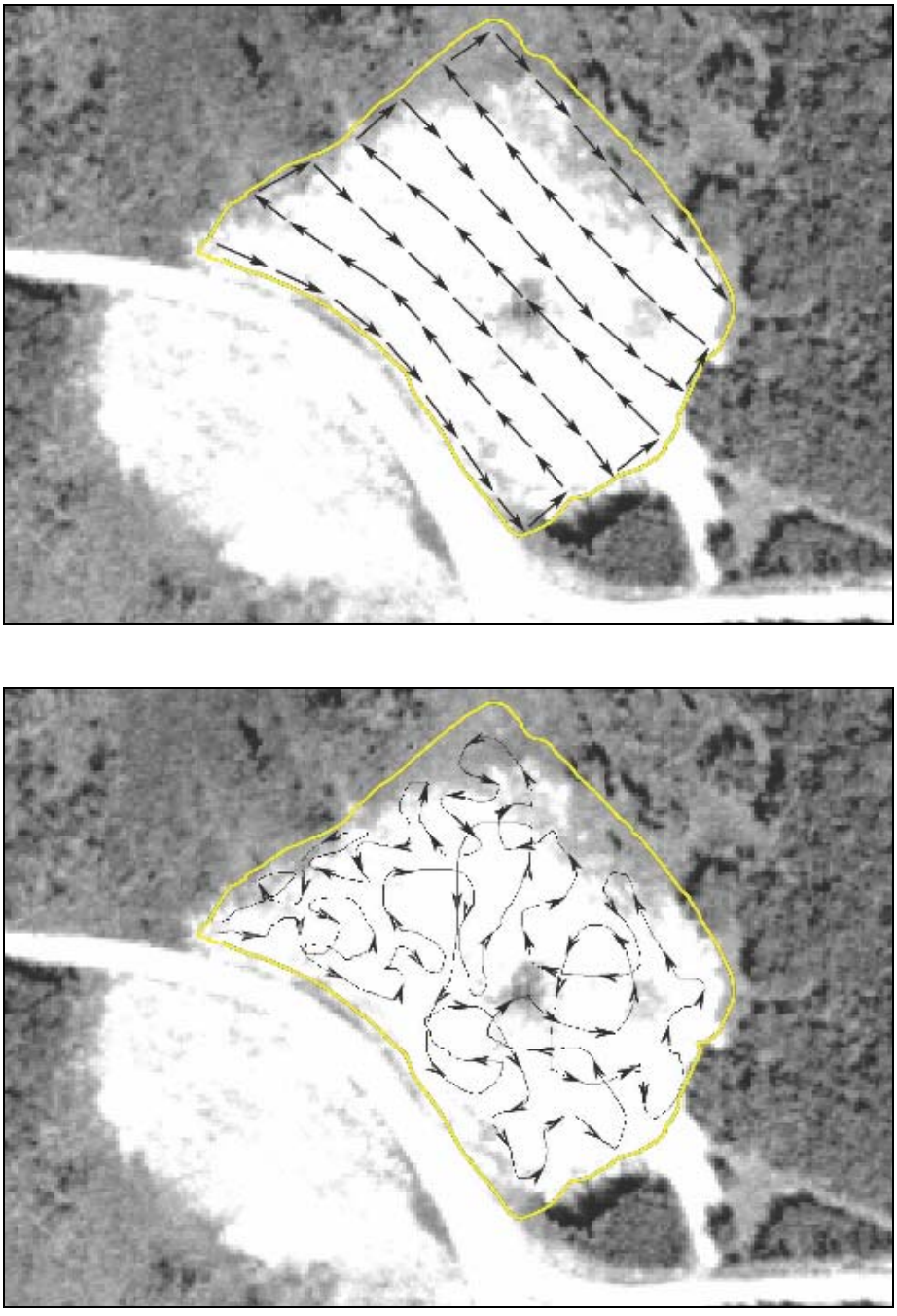

Figure 5. Illustration of sampling methods (systematic random [top] versus random walk [bottom]) used to collect multi-increment samples from a 90-m × 120-m area at FP Mark. For these illustrations, an increment would have been collected at each arrowhead.

FP Sally. FP Sally is located along Meadows Road on the bluff overlooking the Delta River and the Mississippi Impact Area (Fig. 1). According to the DTA Ammunition Reports, 1,285 105-mm high explosives (HE) and illumination (ILL) projectiles had been fired from this area within the previous year, compared to 165 from FP Mark. Unlike FP Mark, the entire surface is heavily vegetated (Fig. 6) and the mineral soil is two to three cm below the surface. Dominant plants are bluegrass (*Poa prantensis*), fireweed (*Epilobium angustifolium),* aspen (*Populus tremuloides*), lingonberry (*Vaccinium vitis-idaea*), and willow (*Salix alaxensis*). The goal of our sampling was to estimate a mean 2,4-DNT concentration to compare to a soil cleanup level, yet we know from past sampling experience that most of the propellant residue resides on the ground surface. As we did at FP Mark, we re-established one of our sampling sites from 2002. At FP Sally, our reconnaissance sample was from an area that was located 50 m directly in front of one of the howitzers where we found 8.8 µg/g 2,4-DNT in a 30-increment sample composed of the top 1-cm fractions of cores. We collected the 2003 reconnaissance sample using a coring device (M.R. Walsh 2004). We collected 10 cores that we divided into three samples based on observable matrix differences: surface vegetation that included the surface interface (similar to the sample from 2002), the root zone, and the subsurface mineral soil. Each sample was extracted with acetone in our field laboratory and the extracts analyzed by GC-TID. The 2,4-DNT concentrations were 7.8 µg/g, 1.2 µg/g, and <d for the surface, root zone, and mineral soil fractions, respectively. After much discussion, we decided that we would be remiss if we collected only subsurface soil when we knew that most of the 2,4-DNT was on the surface organic matter.

With the objective to estimate the mean concentration of 2,4-DNT both at the surface and in the underlying soil over a large area, we collected samples as follows. We marked a 100-m × 100-m area encompassing a part of the firing point where, in 2002, we collected samples 25 m and 50 m in front of a recently fired howitzer and found 2,4-DNT concentrations between 0.23 and 8.8 µg/g (Walsh et al. 2004). For 2003, we had three sampling teams of two where one member used a coring device to obtain a 5-cm-diameter plug sample to a depth of 10 cm and the second member divided the plug at the root zone and placed each division in a separate bag. Each multi-increment sample was composed of approximately 50 increments. Each sampling team systematically traversed the entire 10,000-m^2 area and took a core every 15 paces. Two of the teams collected triplicate samples and one team collected a single sample set, yielding seven sets of surface and subsurface samples.

a. FP Sally.

b. Collection of reconnaissance sample at FP BoWhale.

Figure 6. Vegetated firing points.

FP BoWhale. FP BoWhale is located south of the road to Twin Lakes (Fig. 1 and 6). The surface of the firing point is covered with shrubby vegetation including Potentilla, blueberry (*Vaccinium uliginosum*), cloudberry (*Rubus chamaemorus*), cottongrass (*Eriophorum vaginatum*), and sedge (*Carex bigelowii*). The DTA Ammunition Reports indicated that 277 105-mm HE and ILL projectiles had been fired from this area within the previous year. In 2001, multi-increment samples that we collected 3.5 to 28 m in front of a recently fired howitzer ranged in 2,4-DNT concentration from 1.2 to 27 µg/g.

Prior to marking a 100-m × 100-m area at FP BoWhale, we collected a reconnaissance sample in front of an old howitzer position (indicated by the impression made by the base plate and spade). The multi-increment sample (422 g) was mostly organic matter of which 332 g passed through a 10-mesh sieve. The entire <2-mm fraction of the sample was extracted with acetone and the 2,4-DNT concentration obtained by GC-TID was 0.45 µg/g. We then marked a 100-m × 100-m area and collected some cores to look at the surface stratigraphy. For most of the area, the mineral soil was deeper than the length of our corer. To form our multi-increment samples, we broke each core at the root zone, as we did at FP Sally. The difference at FP BoWhale was that the bottom of the core was organic, not mineral soil. We had three teams of samplers, each of which collected two sets of 50-increment samples, as was done at FP Sally. While we were sampling, the ground was saturated due to 5.4 cm of rainfall within the previous four days, and it was raining while we were sampling.

Field sample collection for estimates of mean NG and 2,4-DNT concentrations at direct fire firing points

Lampkin Firing Point. The Lampkin Range Firing Point is located on an elevated berm that was built on the floodplain of the Delta River (Fig. 1 and 7). This firing point is used for many types of ordnance in addition to 105-mm howitzer (Walsh et al. 2004). The range is a multipurpose testing and training range for firing of small arms, direct fire weapons, and engineer demolitions (USARAK 2002).

We collected duplicate multi-increment samples in 2000 and 2002 and found nitroglycerin (NG) and 2,4-DNT. The results for duplicate field samples were 3.3 and 16.5 µg/g for NG in 2000 and 35 and 59 µg/g in 2002. For 2,4-DNT the duplicate field samples were 0.005 and 0.044 µg/g in 2000 and 0.26 and 0.37 µg/g in 2002. The 2002 samples differed from the 2000 samples in that the samples were larger (larger increments) and the 2002 samples were ground on a ring mill, which may have yielded the improved precision of the concentration estimates for both analytes. Also, the firing point had been used in June 2002 for

a direct fire training with 105-mm howitzers that most likely contributed to the higher concentration of 2,4-DNT in 2002.

Figure 7. Lampkin Range firing point showing partially vegetated gravel berm.

In July 2003, we marked the corners of a 25-m × 90-m area that encompassed most of the top of the firing point berm. Six samplers each collected a multi-increment sample composed of an increment of surface soil (0 to 2.5 cm) collected at approximately 7-m intervals, covering the entire marked area.

Field sample collection for estimates of mean 2,4-DNT concentrations at propellant burn areas

OP7 Propellant Burn Area. Years ago, excess propellant was disposed by burning on the ground. Current practice is to consolidate excess propellant and burn it in a pan (U.S. Army Alaska 2002 [Regulation 350-2]). One of the burn pans for DTA is at Observation Point 7 (OP7) (Fig. 1 and 8).

We collected a reconnaissance multi-increment sample from OP7 in July 2003. Increments of the surface soil were collected within a 10-m-diameter circle around the burn pan. The total sample mass was 745 g. The fraction that was less than 2-mm (562 g) was extracted with acetone and 23 µg/g of 2,4-DNT was determined using the field GC-TID.

a. Collection of reconnaissance sample.

b. Collection of depth sample under corner of burn pan from which rainwater was dripping.

Figure 8. Propellant burn pan located at OP7.

When we returned to OP7 for further sampling, rainwater was dripping from the corner of the pan. We collected 1 L of rainwater as it dripped from the pan and the soil under the drip at 0- to 5-cm, 5- to 10-cm, and 10- to 15-cm depth (Fig. 8b). We also collected multi-increment samples of the surface soils within 8 m of the pan. Increments were collected by random walk to a depth of 5 cm with an AMS #3 scoop.

Also, in May 2003, we collected a surface soil sample under the burn pan on Fort Richardson. This sample was used in a sieve fractionation study described below to determine how 2,4-DNT is distributed between size fractions.

Field sample collection for estimates of 2,4-DNT accumulation at firing points

Resampling of selected 2002 sampling locations. One of our goals in 2002 was to assess the persistence of 2,4-DNT at vegetated and sparsely vegetated firing points. This goal has been complicated by the continued use of firing points for training exercises. However, long-term sampling should reveal whether there is any significant accumulation of 2,4-DNT over time if we are able to adequately minimize the field and laboratory sampling uncertainty. In July 2003, we selected four previously sampled locations at FP Sally (vegetated) and five locations at FP Mark (sparsely vegetated) that represented the range of concentrations that we detected in 2002 (Fig. 3).

In 2002, the 30-increment samples were composed of the top 1 cm of cores from 2-m × 6-m areas. For the resampling in 2003 at vegetated locations, we not only collected the top 1 cm, but, as a separate sample, we collected the top 1 cm of underlying mineral soil (Fig. 9).

Laboratory processing of field samples

General laboratory procedures

All samples from the firing points were air-dried by spreading them on polyethylene-covered trays on shelves in a well-ventilated windowless laboratory. Lights were turned off unless needed to prevent potential photodegradation.

All unvegetated samples were sieved through a #10 mesh (2-mm) sieve and the less-than-2-mm fraction was used to determine analyte concentrations. Some of the unvegetated samples were ground on a ring mill. The model was a Lab-Tech Essa LM-2 equipped with a B800 bowl. The bowl nominally holds 800 g, but current practice is to grind no more than 500 g (Jenkins et al. 2004). Some vegetated samples were ground using a Retsch Impeller-type Cutting Mill Type SM 1.

a. Thirty-increment sample from a 2-m × 6-m area at FP Sally divided into the surface 1 cm and the top 1 cm of the underlying mineral soil.

b. Core from edge of firing point of FP Mark showing organic surface layer and underlying mineral soil.

Figure 9. Samples from vegetated firing points.

If subsampling was performed, the general procedure was to spread the sample over a flat surface and a subsample was formed from several small increments taken from random locations. Some samples were divided using a LabTech Essa Rotary Sample Divider Model RSD5.

Either acetone or acetonitrile was used to extract the analytes from the samples. Acetonitrile is the solvent specified in Methods 8330 (Nitroaromatics and Nitramines by High-Performance Liquid Chromatography [HPLC]) (USEPA 1994) and 8095 (Nitroaromatics and Nitramines by GC) (USEPA 2000) and was used for discrete samples and subsamples of large multi-increment samples. Acetone is used for Methods 8515 (Colorimetric Screening Method for Trinitrotoluene [TNT] in Soil) (USEPA 1996) and 8510 (Colorimetric Screening Procedure for RDX and HMX in Soil). Samples were agitated using a sonic bath or shaker table. Extraction time was 18 hours.

After large multi-increment samples were subsampled, the analyte remaining in the rest of the multi-increment sample was determined using "whole sample extraction." We used acetone for these large-volume extractions because it is less toxic and much less expensive than acetonitrile. It is an excellent solvent for the analytes of interest (2,4-DNT and NG) and it does not cause substantial analytical problems with these late-eluting HPLC analytes. For the whole sample extraction procedure, the sample was weighed and transferred to a large polyethylene carboy. A volume of acetone was added based on the mass of the sample. For each kilogram of sample, 2 L of acetone was added. The carboy was capped and the sample shaken vigorously, then allowed to stand. The sample was shaken vigorously again a few hours later and again the following morning. Then the sample was allowed to stand while the solids settled.

Aliquots of the acetone and acetonitrile extracts were filtered through Millex-FH (Millipore, PTFE, 0.45-µm) filter units into 7-mL Teflon-capped vials. Prior to HPLC analysis, 1.00 mL of filtered extract was mixed with 3.00 mL of MilliQ Water. The HPLC separations were achieved on a 15-cm × 3.9-mm (4-µm) Nova Pak C_8 (Waters Millipore) column eluted with 1.4 mL/minute 15:85 isopropanol:water at 28°C and on a 25-cm by 4.6-mm (5-µm) Supelco LC-CN column eluted with 1.2-mL/minute 65:14:21 water:methanol:acetonitrile. Detection was by UV (254 nm for 2,4-DNT and 210 nm for NG). The analytical precision for the HPLC-UV method was estimated to be 3% relative standard deviation for 2,4-DNT in soils spiked in duplicate at 7.8 µg/g on four separate days (Jenkins and Walsh 1987).

If concentrations were below the HPLC detection limit, filtered extracts were analyzed using gas chromatography and an electron capture detector (USEPA

2000). We used an HP 6890 and a Restek 6-m- × 0.53-mm-id RTX-5ms (95% dimethyl-5% diphenyl polysiloxane) column.

Laboratory processing and subsampling experiments

We performed a variety of experiments to understand why laboratory subsampling error is higher for machine-ground soils with propellant residue compared to machine-ground soils with high explosives residues (Walsh et al. 2002). These experiments included use of a rotary divider to obtain subsamples, use of increased subsample size (up to 900 g), extension of grinding time up to five minutes using a ring mill, sieve analysis to determine the size fraction associated with residues of 2,4-DNT before and after grinding, and use of an acetone-slurry homogenization procedure developed by Defence Research and Development Canada (DRDC) (Thiboutot et al. 1998). We also used a cutting mill to process organic samples from the vegetated firing points. Details of each of the experiments are described with the corresponding results in this report. Some of the multi-increment samples were used for subsampling experiments; however, for all multi-increment soil samples, all soil that was less than 2 mm was extracted and the concentrations reported are based on the total mass and total 2,4-DNT mass determined in the less-than-2-mm fraction of each soil sample.

Spiked Ottawa sand samples

Based on past experience of poor subsampling precision of firing point samples, we hypothesized that the 2,4-DNT was associated with nitrocellulose fibers that did not grind sufficiently in a ring mill within 60 seconds. To test this hypothesis we spiked two 500-g portions of Ottawa Sand. One portion was spiked with a fiber of M1 Propellant and the other with a grain of Standard Analytical Reference Material (SARM) 2,4-DNT. Each spiked sample was ground on the ring mill for 60 s and twelve 10-g subsamples taken for analysis. Then the remainder of the sample was further ground for another four minutes and twelve 10-g subsamples were taken for analysis.

3 RESULTS

Field sample collection methods

10-m × 10-m grid at FP Mark

No laboratory subsampling was performed on the less-than-2-mm fraction of the discrete samples from the 10-m × 10-m grid. The fractions ranged in mass from 39 to 82 g and were extracted with acetonitrile using a shaker table.

Concentrations of 2,4-DNT in the 100 discrete samples (Fig. 10) ranged from 0.0007 to 6.4 µg/g (Table 1). The data did not form a linear array on a normal probability plot (Fig. 11), indicating that the mean is not a suitable measure of the central tendency of the data representing 2,4-DNT concentrations in discrete samples. The frequently used practice of comparing the 95% upper confidence limit of the arithmetic mean to a cleanup level is not statistically valid. Also, the short-range heterogeneity was large, as shown by the scatter plot (Fig. 12) of the 20 paired discrete samples collected within 1-m × 1-m cells. There was no correlation between the 2,4-DNT concentrations in the discrete samples that were essentially co-located. Overall, individual discrete samples are too small to represent the matrix that we are attempting to characterize (e.g., 2,4-DNT in the top 2.5 cm of soil). However, the 120 discrete samples, if treated as a single sample, may be of adequate sample size to estimate the mean concentration in the 10-m × 10-m grid. The total mass of the less-than-2-mm fraction of soil for the 120 discrete samples was 6,860 g and the total mass of 2,4-DNT detected in the extracts was 6,770 µg, yielding an estimated 2,4-DNT soil concentration of 0.99 µg/g.

By treating the 120 discrete samples as a single sample, we are essentially forming a multi-increment sample. Pooling of an adequate number of individual samples to form multi-increment samples can provide normally distributed estimates of mean concentration. The data from the 10 30-increment samples that we collected from the 10-m × 10-m grid do form a linear array on a normal probability plot (Fig. 13). The mean and median concentrations of 2,4-DNT were nearly equivalent (0.93 µg/g and 0.90 µg/g) (Table 1), as would be expected for normally distributed data, and were very close to the 2,4-DNT concentration obtained by combining the 120 discrete samples (0.99 µg/g). The masses of the less-than-2-mm fraction ranged from 1660 to 2,440 g and the total soil mass analyzed was 21,300 g, or approximately three times that of the 120 discrete samples. A standard deviation and 95% upper confidence limit were computed

from normally distributed data from the replicate multi-increment samples (Table 1) (EPA 1992):

$$UL_{1-\alpha} = \text{mean} + t_{1-\alpha,\, n-1}\,(s/n^{0.5}) = (0.93 + 0.14)\ \mu g/g = 1.07\ \mu g/g$$

$$t_{0.95,\, 9} = 1.833. \qquad (1)$$

The 2,4-DNT data for 10-increment samples from 20 of the 1-m × 1-m cells within the 10-m × 10-m grid were also normally distributed (Fig. 14). The mean and median 2,4-DNT concentrations were 0.94 and 0.96 µg/g (Table 1), respectively. The upper confidence limit for the mean was 1.08 µg/g. The total mass of soil (<2 mm) collected was 15,220 g and the total mass of 2,4-DNT was 14.16 mg. The similarity in the distribution of these data with that from the entire 10-m- × 10-m-grid multi-increment samples indicates that the scale of heterogeneity is similar over a 1-m^2 area to that of the 100-m^2 area.

Total mass of soil (<2 mm) collected from the 10-m × 10-m grid was 43.4 kg and the total mass of 2,4-DNT extracted from this soil was 40.5 mg, yielding an estimated 2,4-DNT concentration of 0.93 µg/g.

Multi-increment samples from 90-m × 120-m area at FP Mark

The next set of samples we collected was used to estimate the mean 2,4-DNT concentration over a larger area. We tested the effect of the number of increments (50 versus 200), the sampler's individual technique, and the randomness of the locations of the increments.

Table 2 lists the 2,4-DNT concentrations determined in the various multi-increment samples from a 90-m × 120-m area at FP Mark. In total, 116.6 kg of soil (less than 2 mm) was analyzed, and the sum of the 2,4-DNT mass found was 59.5 mg, yielding an estimated 2,4-DNT concentration of 0.51 µg/g. The single sampler that collected six 50-increment samples and one 100-increment sample using a systematic random (Fig. 5) sampling scheme yielded an estimated mean 2,4-DNT concentration of 0.47 µg/g with a relative standard deviation of 18%. The other samplers that collected 50-increment and 200-increment samples using the systematic random sampling scheme yielded estimated mean 2,4-DNT concentrations that were nearly identical (0.59 and 0.56 µg/g) and had similar relative standard deviations (22% and 25%). There was no advantage to increasing the number of increments from 50 to 200. The ratio of the variances between the multiple samplers versus the single sampler was not significant ($F = 2.44$, $F(4, 6) = 4.54$) at the 95% confidence level.

Cell 91 0.97	Cell 92 2.72, 2.10* 0.80†	Cell 93 0.26	Cell 94 3.88	Cell 95 1.18	Cell 96 0.32, 1.01* 0.96†	Cell 97 0.0007	Cell 98 0.44	Cell 99 0.004	Cell 100 0.002
Cell 81 0.07	Cell 82 1.59	Cell 83 0.36	Cell 84 0.04	Cell 85 0.27	Cell 86 0.03	Cell 87 0.11	Cell 88 0.50	Cell 89 0.07	Cell 90 0.58
Cell 71 1.86	Cell 72 3.44	Cell 73 0.23	Cell 74 1.03, 0.60* 0.79†	Cell 75 0.15	Cell 76 0.13	Cell 77 0.18, 0.45* 0.76†	Cell 78 1.37	Cell 79 0.57	Cell 80 1.06, 0.22* 0.33†
Cell 61 0.71	Cell 62 0.68	Cell 63 4.78	Cell 64 3.38	Cell 65 2.39	Cell 66 0.01, 0.73* 0.95†	Cell 67 0.24	Cell 68 0.63	Cell 69 0.001	Cell 70 0.002, 0.13* 0.96†
Cell 51 0.59	Cell 52 1.22, 0.61* 0.78†	Cell 53 1.13	Cell 54 0.87	Cell 55 0.66	Cell 56 0.26	Cell 57 1.62	Cell 58 0.15, 0.10* 1.03†	Cell 59 0.61	Cell 60 0.008
Cell 41 0.96	Cell 42 1.06	Cell 43 3.08	Cell 44 1.64	Cell 45 0.27	Cell 46 1.95, 0.80* 1.27†	Cell 47 0.36	Cell 48 0.06	Cell 49 0.93	Cell 50 0.67
Cell 31 1.68	Cell 32 0.18	Cell 33 1.00	Cell 34 1.05, 0.65* 1.10†	Cell 35 2.68, 0.20* 1.30†	Cell 36 1.74	Cell 37 0.37, 1.41* 1.16†	Cell 38 0.29	Cell 39 3.45, 1.71* 1.37†	Cell 40 1.51
Cell 21 1.52	Cell 22 1.96	Cell 23 1.07	Cell 24 0.51	Cell 25 4.18	Cell 26 0.058	Cell 27 1.13, 0.15* 0.73†	Cell 28 0.02, 0.19 1.72†	Cell 29 0.35	Cell 30 1.83
Cell 11 0.40	Cell 12 0.66, 1.49* 0.92†	Cell 13 0.19	Cell 14 1.71	Cell 15 6.38	Cell 16 2.00	Cell 17 0.41	Cell 18 0.34	Cell 19 0.18, 0.22* 0.47†	Cell 20 1.15
Cell 1 2.71	Cell 2 0.65	Cell 3 0.56	Cell 4 1.60	Cell 5 1.26	Cell 6 1.25	Cell 7 2.63, 1.05* 1.09†	Cell 8 0.63, 0.01* 0.24†	Cell 9 0.18	Cell 10 0.19

*Duplicate discrete sample.

†10-increment sample.

Figure 10. Cell ID numbers and 2,4-DNT concentrations (µg/g) in discrete samples and 10-increment samples from 1-m × 1-m cells within a 10-m × 10-m grid at FP Mark. Duplicate discrete samples and the 10-increment samples were collected from 20 randomly chosen cells.

Table 1. Summary statistics for 100 discrete samples and 10 30-increment samples collected within a 10-m × 10-m gridded area at FP Mark and for 20 10-increment samples from 20 randomly selected 1-m^2 cells within the 100-m^2 grid. Individual discrete samples were taken from within 1-m × 1-m cells and the multi-increment samples were composed of soil increments from random locations. Data for individual samples are in Appendix A.

Type of sample	Discrete	10-m × 10-m grid 30-increment sample	1-m × 1-m cell 10-increment sample
Number of samples	100	10	20
Mean concentration	1.1 µg/g*	0.93 µg/g	0.94 µg/g
Median	0.65 µg/g*	0.90 µg/g	0.96 µg/g
Minimum concentration	0.0007 µg/g	0.60 µg/g	0.24 µg/g
Maximum concentration	6.4 µg/g	1.35 µg/g	1.72 µg/g
Standard deviation		0.25 µg/g	0.35 µg/g
95% upper confidence limit		0.93 + 0.14	0.94 + 0.14

* The mean for the 100 discrete samples is not an appropriate measure of the central tendency of these data. These data are not normally distributed (Fig. 11).

The random walk sampling scheme (Fig. 5) yielded an estimated 2,4-DNT concentration of 0.41 µg/g with a relative standard deviation of 28%. However, there was a significant difference between the samplers at the 95% confidence level. (Using Analysis of Variance, the calculated F value was 6.05, which is greater than $F_{(2, 6)} = 5.14$.)

Based on the above results, the systematic random sample collection method is recommended. The 50-increment sample was sufficient to estimate the mean 2,4-DNT concentration with a relative standard deviation of 25% or less. Replication of field samples by each sampler using the systematic random sample collection should be performed to determine if biases are introduced by sampling technique.

Multi-increment samples from FP Sally and FP BoWhale

The results from the 100-m × 100-m areas at FP Sally and FP BoWhale illustrate the difficulty of reproducibly collecting samples from heavily vegetated firing points (Table 3). The range of 2,4-DNT concentrations for the seven surface multi-increment samples at FP Sally was 0.14 to 3.7 µg/g and the median was 1.55 µg/g. The range of 2,4-DNT concentrations for similarly collected surface samples at FP BoWhale was 0.97 to 5.65 µg/g and the median was 2.1 µg/g. These unacceptably large ranges in estimated concentrations indicate that

we did not collect a sufficient number of increments or enough mass of the vegetated matrix. Differences in sampling technique, especially with respect to depth, may have contributed to the sampling error.

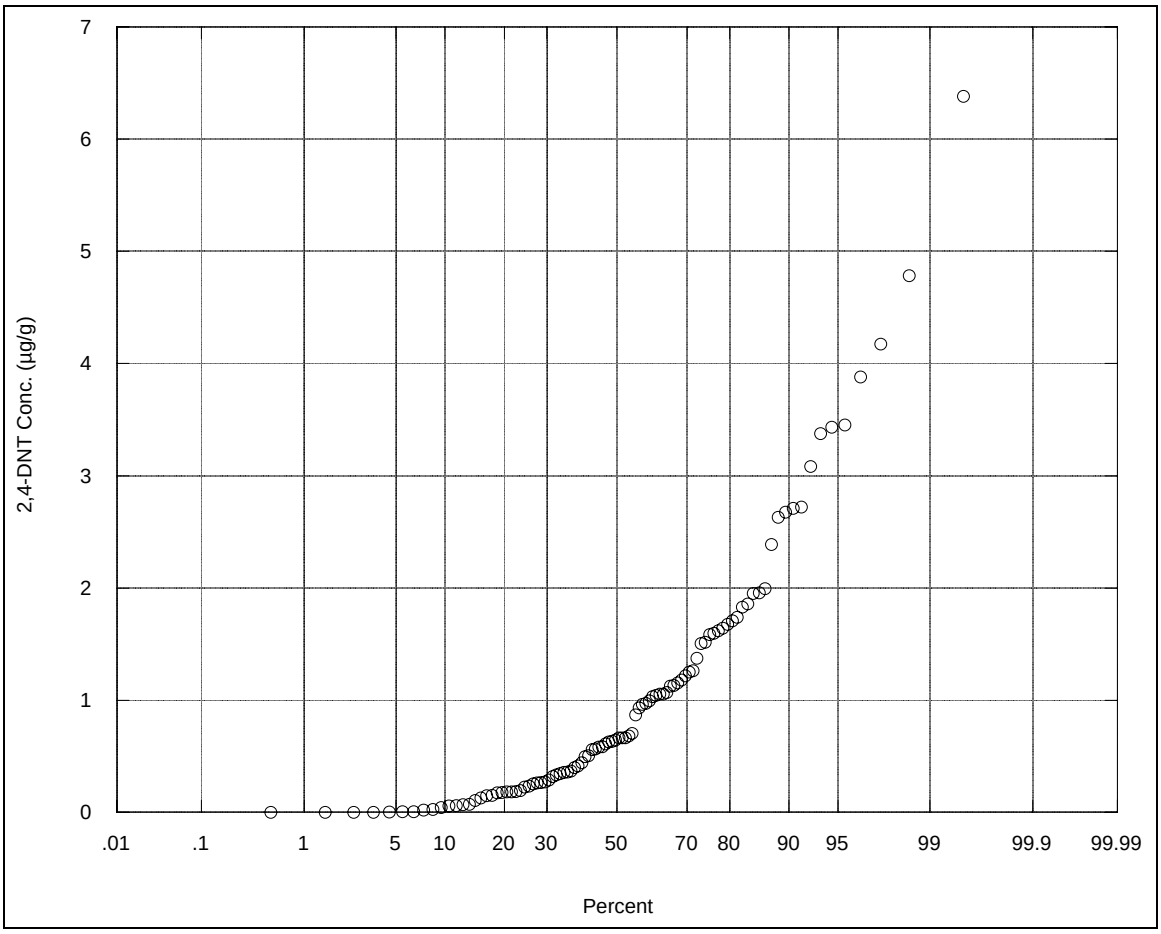

Figure 11. Normal probability plot for 100 discrete simplexes collected from a 10-m ×10-m area at FP Mark.

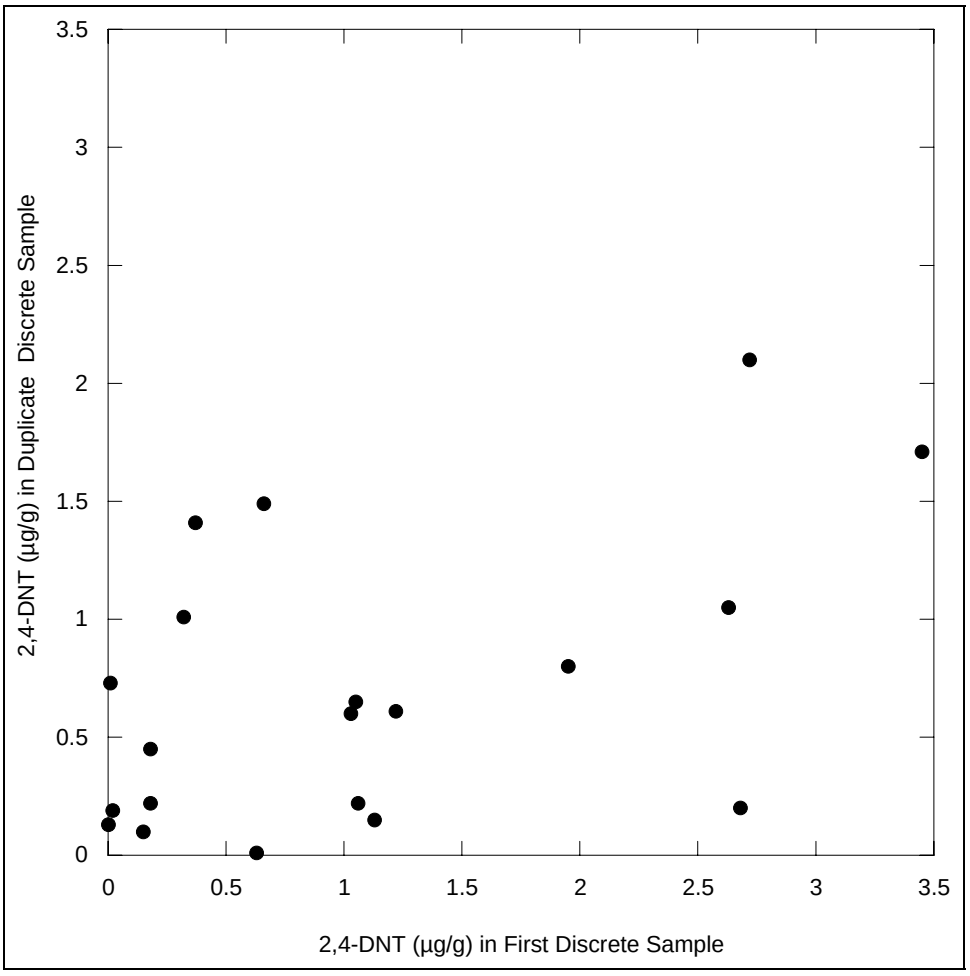

Figure 12. Scatter plot of 2,4-DNT concentrations found in duplicate discrete samples collected within 1-m × 1-m areas at FP Mark.

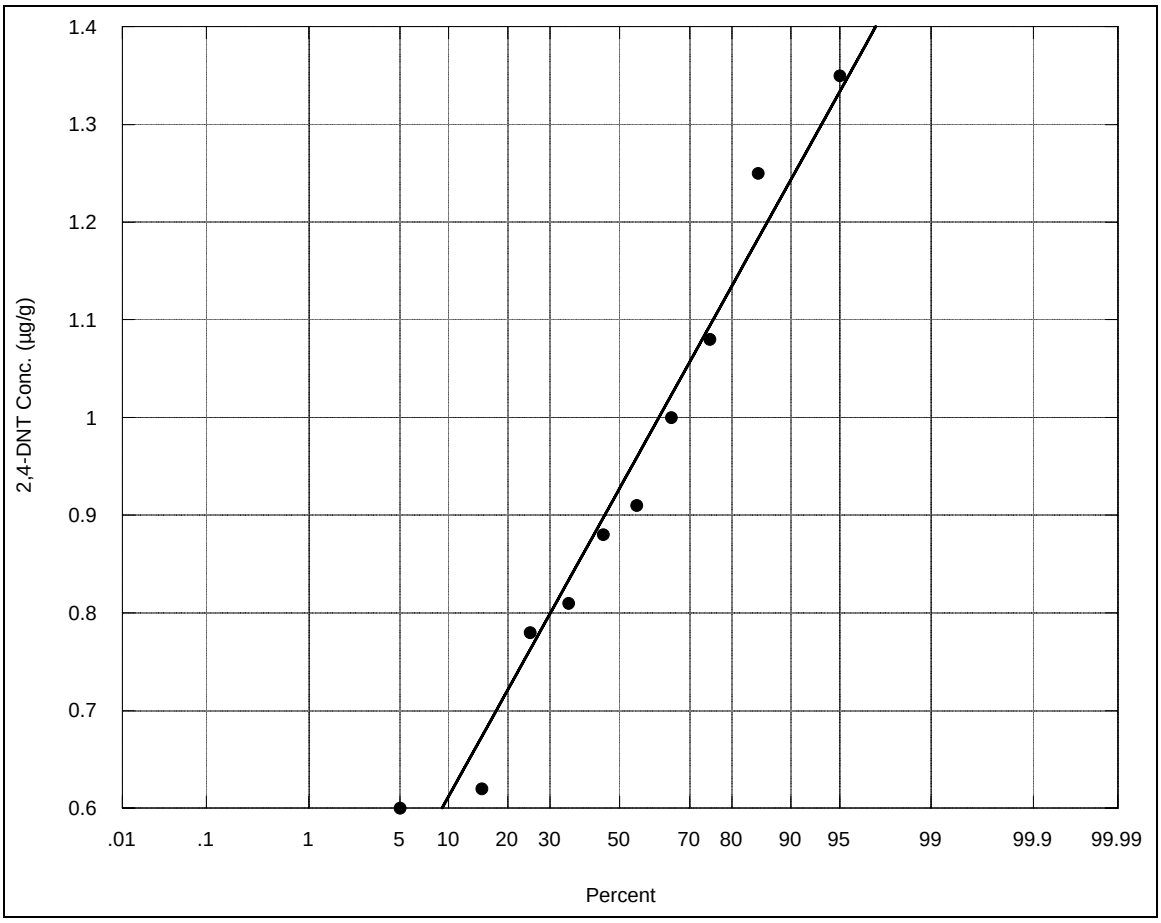

Figure 13. Normal probability plot for 10 30-increment samples from a 10-m × 10-m area at FP Mark. Increments were taken from random locations.

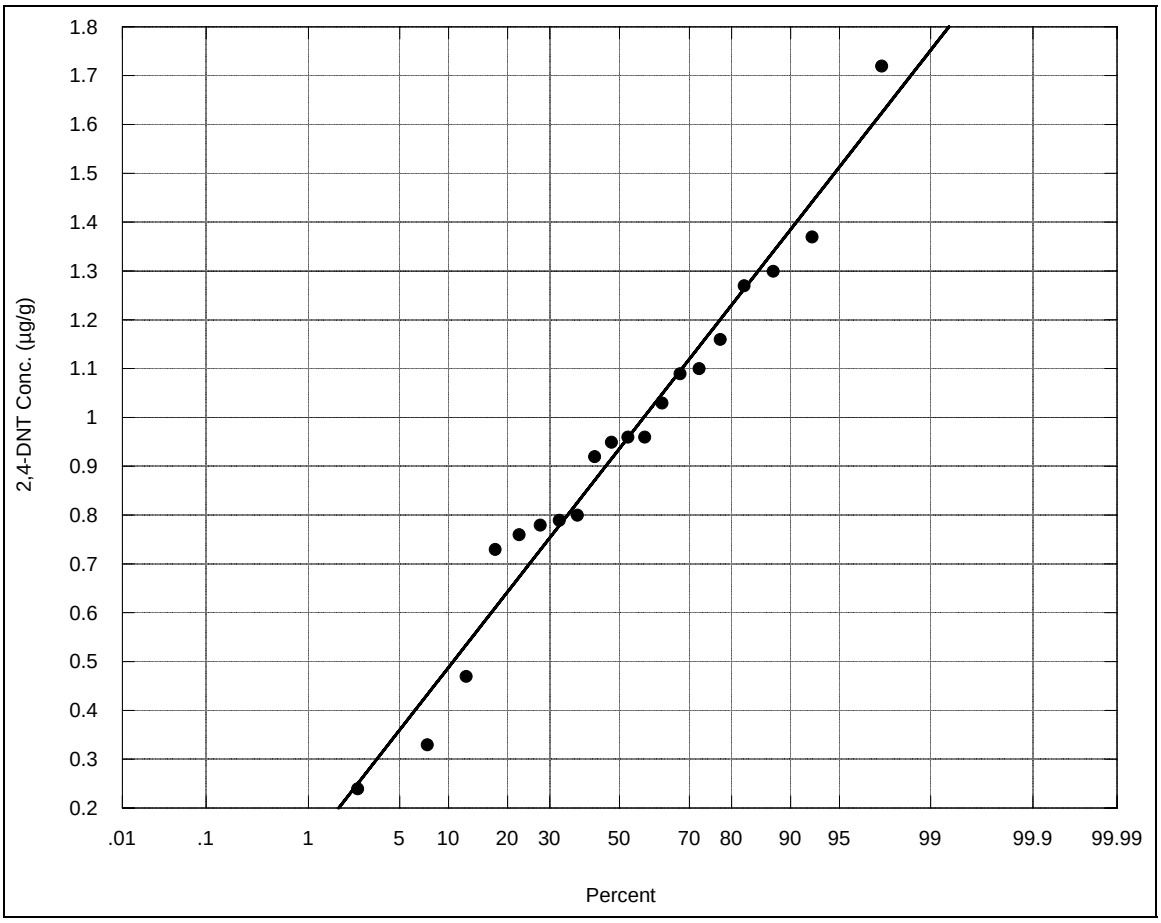

Figure 14. Normal probability plot for 20 10-increment samples from 1-m × 1-m cells within the 10-m × 10-m grid at FP Mark.

Table 2. 2,4-DNT concentrations determined for 50- to 200-increment samples from a 90-m × 120-m area at FP Mark. Total soil mass (<2 mm) was 116.6 kg and total 2,4-DNT mass was 59.5 mg, yielding an estimated 2,4-DNT concentration of 0.51 µg/g.

Sample ID	Mass <2 mm (kg)	Sampler	Actual number of increments	2,4-DNT (µg/g)
50 to 100 increments, single sampler, systematic random				
FP151	5.72	CAR	100	0.50
FP152	3.15	CAR	50	0.42
FP153	3.17	CAR	50	0.56
FP154	3.41	CAR	50	0.54
FP155	3.27	CAR	50	0.42
FP184	3.61	CAR	50	0.32
FP185	3.11	CAR	50	0.50
			Mean	0.47
			Variance	0.00698
			RSD	18%
			95% UCL	0.53
50 increments, multiple samplers, systematic random				
FP164	3.33	CMC	45	0.70
FP165	2.72	ADH	45	0.62
FP166	2.69	KB	54	0.43
FP167	2.74	MEW	47	0.73
FP168	3.44	MRW	54	0.49
			Mean	0.59
			Variance	0.0170
			RSD	22%
			95% UCL	0.73
200 increments, multiple samplers, systematic random				
FP179	9.85	KB	239	0.58
FP180	10.95	ADH	210	0.76
FP181	9.72	CMC	200	0.59
FP182	11.48	MRW	200	0.40
FP183	12.34	MEW	200	0.46
			Mean	0.56
			Variance	0.0192
			RSD	25%
			95% UCL	0.71

Table 2 (cont'd). 2,4-DNT concentrations determined for 50- to 200-increment samples from a 90-m × 120-m area at FP Mark. Total soil mass (<2 mm) was 116.6 kg and total 2,4-DNT mass was 59.5 mg, yielding an estimated 2,4-DNT concentration of 0.51 µg/g.

Sample ID	Mass <2 mm (kg)	Sampler	Actual number of increments	2,4-DNT (µg/g)
50 increments, random walk, replicate samplers				
FP226	3.28	MEW	55	0.36
FP227	3.01	MEW	49	0.30
FP228	2.76	MEW	50	0.26
FP229	2.06	MRW	50	0.27
FP230	1.89	MRW	50	0.50
FP231	2.14	MRW	51	0.43
FP232	2.24	CMC	50	0.53
FP233	2.33	CMC	50	0.52
FP234	2.20	CMC	50	0.50
			Mean	0.41
			Variance	0.0126
			RSD	28%
			95% UCL	0.48

At FP Sally, the subsurface samples were mineral soil and 2,4-DNT was not detectable in six of the seven samples. In contrast, the subsurface samples at FP BoWhale were organic and 2,4-DNT was detectable in five of the six subsurface samples. In all but one sample, the concentration was much less than that found on the surface.

Multi-increment samples from Lampkin Range Firing Point

The Lampkin Range firing point presented another challenging surface to sample. The firing point is a gravel berm that is partially vegetated (Fig. 7). Each of the six multi-increment samples contained NG, probably from training with mortars and 40-mm rifle grenades, as well as 2,4-DNT from 105-mm howitzers.

The difficulty in sampling the gravelly substrate is reflected in the wider range of masses of the multi-increment samples, from less than 2 kg to greater than 3 kg (Table 4) for the less-than-2-mm fraction. The range of 2,4-DNT concentrations was 0. 25 to 1.02 µg/g, and the mean was 0.55 µg/g with a relative standard deviation of 58%. The range of NG concentrations was 1.7 to 10.3 µg/g, and the mean was 4.56 µg/g with a relative standard deviation of 68%.

These relative standard deviations are higher than desired and may reflect distributions that depart somewhat from normality.

Table 3. 2,4-DNT concentrations in surface and subsurface multi-increment samples collected for vegetated firing points. The sets of multi-increment samples were from 100-m × 100-m areas at each firing point. 2,4-DNT concentrations are based on whole sample extractions.

Lab ID numbers Surface/ subsurface	Mass of samples (kg) Surface/ subsurface	Samplers	Actual number of increments	2,4-DNT (µg/g)	
				Surface	Subsurface
FP Sally					
FP186/FP190	1.73/2.15	CAR and ADH	42	1.07	not detected
FP188/FP192	1.73/2.36	CAR and ADH	42	0.14	not detected
FP222/FP225	2.15/2.77	CAR and ADH	49	0.45	not detected
FP187/FP191	1.42/2.16	KB and CMC	49	3.70	not detected
FP189/FP193	1.98/2.50	KB and CMC	49	1.75	not detected
FP221/FP224	2.12/2.41	KB and CMC	49	1.55	not detected
FP220/FP223	2.33/2.21	MEW and MRW	49	1.74	0.23
FP BoWhale					
FP210/FP216	1.90/1.35	CAR and ADH	49	1.50	0.02
FP211/FP217	2.12/1.73	CAR and ADH	49	0.97	not detected
FP212/FP218	1.38/1.05	KB and CMC	42	1.88	1.19
FP213/FP219	1.40/1.63	KB and CMC	49	2.22	0.15
FP208/FP214	1.92/2.40	MEW and MRW	56	2.49	0.10
FP209/FP215	1.49/1.63	MEW and MRW	49	5.65	0.24

Multi-increment samples from OP7 Propellant Burn Area

Designated propellant burn locations equipped with burn pans have replaced the former practice of burning excess propellant on the ground surface at the firing point. Use of designated burn locations permits some control over the release of potentially hazardous chemicals.

The burn pan at OP7 is simply a metal box with a hinged lid (Fig. 8). Scorched trees on one side of the observation point were evidence of the intense heat from propellant burning. Multi-increment samples collected within 8 m of the burn pan had 2,4-DNT concentrations about one order of magnitude higher than at FP Mark and the relative standard deviation was similar to that at FP Mark (Table 5). The relative standard deviation for the mean NG concentration was 44%, mostly due to one sample.

Table 4. Concentrations (µg/g) of 2,4-DNT and NG in multi-increment samples from Lampkin Range firing point. Concentrations are based on whole sample extractions.

Lab ID	Mass <2-mm fraction (kg)	Sampler	Actual number of increments	2,4-DNT (µg/g)	NG (µg/g)
FP202	2.62	MEW	42	1.02	1.7
FP203	1.82	ADH	42	0.52	10.3
FP204	2.13	MRW	42	0.37	3.21
FP205	1.76	KB	47	0.25	5.34
FP206	3.36	CAR	44	0.29	2.44
FP207	2.22	CMC	45	0.86	4.34
			Mean	0.55	4.56
			s	0.32	3.10
			RSD	58%	68%
Moss (0.45 kg): 2,4-DNT 0.53 µg/g					

Table 5. Concentrations (µg/g) of 2,4-DNT and NG in multi-increment samples from OP7 where excess propellant is burned in a pan. Concentrations are based on whole sample extractions.

Lab ID	Mass <2-mm fraction (kg)	Sampler	Actual number of increments	2,4-DNT (µg/g)	NG (µg/g)
FP170	2.55	CAR	35	10.2	5.20
FP171	3.42	MRW	40	10.0	2.34
FP172	3.21	CMC	40	10.1	2.23
FP173	2.82	MEW	35	7.85	2.44
FP174	2.43	KB	33	5.38	1.92
FP175	2.32	ADH	40	5.76	2.51
			Mean	8.22	2.78
			s	2.23	1.21
			RSD	27%	44%
			Upper CL (95%)	8.22 + 1.83	2.78 + 0.99

Multi-increment samples from 2002 locations

In 2003, we revisited four locations at FP Sally and five locations at FP Mark that we sampled in 2002 to assess persistence and accumulation of 2,4-DNT. Each location was a 2-m × 6-m area at a known distance and angle from a howitzer that was fired in June 2002. Both firing points were used for training in August 2002 before two samples were collected in September 2002 from locations that had the highest concentrations in June and July 2002. Both firing points were used over the winter; many more projectiles were fired from FP Sally than

from FP Mark. In 2003, we separated each core from vegetated locations into the surface 1 cm and the top 1 cm of mineral soil (Fig. 9).

Of the five FP Mark locations, three were vegetated; two were at the edge of the firing point and the third was a shrubby vegetated island in the middle of the firing point. The iterative sampling at FP Mark did not reveal any significant accumulation in the surface 1 cm. However, each subsurface sample at FP Mark had detectable concentrations of 2,4-DNT (Table 6).

Table 6. Resampling of previously sampled locations at FP Mark and FP Sally to access accumulation of 2,4-DNT residue. 2,4-DNT concentrations are estimated from solvent extraction of the entire field samples without subsampling.

	2,4-DNT (µg/g)			
Sample ID	**June 2002**	**July 2002**	**September 2002**	**July 2003**
Mark2 0° 50-m	1.10	0.71		0.97
Mark2 60R 50-m	0.62	0.57		1.07
Mark2 30R 25-m surface	1.88	3.04		2.17
Mark2 30R 25-m subsurface soil				4.30
Mark2 30R 95-m surface	6.86	5.70		8.62
Mark2 30R 95-m subsurface soil				2.03
Mark2 60R 100-m surface	19.6	23.2	17.3	11.8
Mark2 60R 100-m subsurface soil				0.88
Sally5 0° 10-m surface	8.67	3.32		10.4
Sally5 0° 10-m subsurface soil				not detected
Sally5 30R 25-m surface	0.44	0.51		1.59
Sally5 30R 25-m subsurface soil				not detected
Sally5 30L 50m Surface	0.12	0.12		1.31
Sally5 30L 50m Subsurface Soil				not detected
Sally5 60L 10m Surface	12.2	3.50	8.10	9.76
Sally5 60L 10m Subsurface Soil				not detected

At FP Sally, one of the locations appeared to have significantly more 2,4-DNT than in 2002 (order of magnitude more), one appeared to have a slight increase in concentration, and two appeared to be about the same (less than a factor of two difference). No 2,4-DNT was detectable in the subsurface soil.

If the 2,4-DNT concentrations at the firing points will be monitored in the long term, the area sampled needs to be sufficiently large to represent a significant part of the firing point. For FP Mark, 50-increment samples yielded estimates of 2,4-DNT concentrations that were normally distributed and the

relative standard deviation was 25% or less. Increased number of increments and mass per multi-increment sample at FP Sally and FP BoWhale should improve the accuracy and precision of estimates of the mean 2,4-DNT concentrations at these vegetated firing points.

Laboratory processing and subsampling experiments

Splitting of an unground multi-increment sample

The 200-increment samples from FP Mark were approximately 10 kg (<2-mm fraction). Our first subsampling experiment was to see whether we could split a large sample and use only a portion for further processing. Of the methods available for dividing a large particulate sample (i.e., cone-and-quartering, fractional shoveling, chute riffling, spinning riffling), the spinning riffle sample divider is recognized as the least likely to discriminate with respect to size, density, or other particle characteristics. We used a Labtech Essa Rotary Sample Divider (Model RSD5) to divide one of the 200-increment samples from FP Mark (FP180). The divider is composed of a hopper, vibratory feeder, and a rotating turntable containing 12 receiving sectorial buckets. When we split the 10.95 kg sample into 12 subsamples, the relative standard deviation for the subsample masses was 2.7% (Table 7). Each approximately 900-g subsample was extracted with acetone, and we determined the 2,4-DNT concentrations. The concentrations ranged from 0.50 to 1.28 µg/g, the mean was 0.76 µg/g and the relative standard deviation was 28%. This subsampling variability would have compromised our study of the reproducibility of field samples. These results demonstrate that even under ideal laboratory conditions, reduction in sample volume by splitting or subsampling is a major source of error. Splitting samples under field conditions is not recommended because the subsampling error will be significantly larger.

Effect of grinding using a ring mill on the variance of mean 2,4-DNT concentrations

Multi-increment samples from FP Mark were used to study why 60 s of grinding on a ring mill was not sufficient to reduce the subsampling error associated with 2,4-DNT propellant residue.

We used the ten-increment samples collected from individual cells to measure subsampling error associated with 2,4-DNT before and after machine grinding. The less-than-2-mm fraction for 14 of the samples was spread on a flat surface and duplicate 10-g subsamples formed by manually taking at least 30 small increments of soil. Then the rest of the sample was ground for 60 seconds

on a LabTech Essa LM-2 Ring Mill, and another set of 10-g subsamples collected. Table 8 shows the results of duplicate 10-g subsamples taken before and after grinding and the 2,4-DNT concentration found by whole sample extraction in the remaining sample. Without question, the subsampling error was unacceptably high before and after grinding. We used a rotary divider for two samples (FP124 and FP130) to see if machine division using a rotary divider and larger subsamples (~60 g), would improve precision (Table 9), but subsampling error remained high.

Table 7. Variability in subsample masses and 2,4-DNT concentrations after rotary division of a 200-increment sample (FP180) from FP Mark. 2,4-DNT was determined in each split following whole sample extraction.

Split	Mass (g)	2,4-DNT (µg)	2,4-DNT concentration (µg/g)
1	871	799	0.92
2	907	768	0.85
3	908	595	0.66
4	909	460	0.51
5	889	689	0.78
6	952	659	0.69
7	940	841	0.90
8	897	1,150	1.28
9	942	703	0.75
10	934	464	0.50
11	883	535	0.61
12	920	664	0.72
Sum	10,952	8,330	
Mean	913		0.76
s	25		0.21
RSD	2.7%		28%
median	909		0.735

Table 8. Estimates of 2,4-DNT concentrations in 10-g subsamples of multi-increment samples from cells of the 10-m × 10-m grid at FP Mark before and after grinding for 60 s then extracting the remaining sample. Each subsample was obtained manually and was 10.0 g.

		2,4-DNT concentration (µg/g)				2,4-DNT (µg/g)	
		Before grinding		After grinding			
Lab ID	Position in grid	A	B	C	D	Whole sample extraction	Mass of soil remaining (kg)
FP121	Cell 007	3.52	1.57	0.56	1.37	0.99	0.72
FP123	Cell 012	4.95	0.33	1.16	1.10	0.79	0.56
FP124	Cell 019	0.59	0.08	0.10	0.91	0.47*	0.68
FP125	Cell 027	5.70	0.10	0.08	0.48	0.68†	0.70
FP126	Cell 028	0.07	4.90	0.28	0.25	1.64	0.71
FP129	Cell 037	1.54	0.34	0.95	1.51	1.09	0.63
FP130	Cell 039	0.73	0.23	1.63	0.11	1.4*	0.74
FP131	Cell 046	1.56	3.34	1.49	2.12	1.2	0.90
FP132	Cell 052	0.56	0.38	0.93	0.33	0.75	0.71
FP133	Cell 058	0.07	0.86	1.06	0.10	1.05†	0.76
FP135	Cell 070	0.01	0.03	2.54	7.06	0.87	1.07
FP137	Cell 077	0.04	0.02	1.71	0.43	0.73	0.85
FP138	Cell 080	0.01	0.01	0.01	0.01	0.33	1.02
FP139	Cell 092	0.02	2.76	0.32	0.80	0.81†	0.75
FP140	Cell 096	0.02	0.10	0.44	0.41	0.95	0.80

* Rotary division (Table 9)

† Further grinding (Table 10)

Table 9. Estimates of 2,4-DNT in four of 12 splits obtained using a rotary division of two ground (60 s) multi-increment samples from cells of the 10-m × 10-m grid at FP Mark. The remaining eight splits for each sample were combined and 2,4-DNT concentration determined without subsampling.

FP124 Cell 19			FP130 Cell 39		
Split	**Mass (g)**	**2,4-DNT (µg/g)**	**Split**	**Mass (g)**	**2,4-DNT (µg/g)**
5	62.5	0.35	4	58.6	1.1
6	66.0	0.41	5	57.9	0.61
10	47.0	0.66	7	62.6	2.34
11	58.6	0.20	12	54.7	1.26
	Mean	0.41		Mean	1.33
	s	0.19		s	0.73
	RSD (%)	47%		RSD (%)	55%
Split	Mass (g)	2,4-DNT (µg/g)	Split	Mass (g)	2,4-DNT (µg/g)
All remaining splits	450	0.51	All remaining splits	503	1.43

We hypothesized that the 2,4-DNT was associated with fibers of nitrocellulose-based propellant and that longer grinding times may be necessary to reduce the fiber size sufficiently for precise subsampling. However, longer grind times generate heat that could result in analyte loss. We performed a series of experiments to study the effect of grinding times on 2,4-DNT propellant residues.

First, we ground three samples (FP125, FP133, and FP139) that had poor subsampling precision (Table 8) for two additional two-minute intervals and manually obtained triplicate 10-g subsamples from each sample after each grind. Then we extracted the remaining soils. The lowest RSD (%) was for FP125 after an additional two minutes of grinding (Table 10); however, the mean 2,4-DNT concentration doubled for the triplicate 10-g subsamples after an additional two minutes of grinding (total of five minutes) and was similar to the concentration for the remaining 642 g of the sample. These results imply that at least one propellant fiber was not adequately ground after three minutes of grinding. The additional grinding reduced the subsampling variance for the other two samples (FP133 and FP139) (Table 10).

To further explore the effect of grind time on subsampling variance, we divided one of the 30-increment samples (FP150) from the 10-m × 10-m grid into three splits using the rotary divider. One split was ground for one minute, the second for three minutes, and the third for five minutes. The ground samples were then divided into 12 subsamples using the rotary divider. The subsamples

were approximately 60 g each. The results from this experiment (Table 11) show that 60 s is an inadequate grind time and that extended grinding for five minutes reduced the subsampling variance. However, the subsampling error was greater than the error associated with ground HE-contaminated soils, which is typically less than 5% RSD.

Table 10. Estimates of 2,4-DNT in manually collected 10-g subsamples of multi-increment samples from cells of the 10-m × 10-m grid at FP Mark after grinding for two 2-minute intervals. Triplicate 10-g subsamples were taken for analysis after each grind cycle, then 2,4-DNT concentrations were determined in the remainder of each sample without subsampling.

	2,4-DNT concentration (µg/g)		
Replicate (10 g)	**FP125 Cell 27**	**FP133 Cell 58**	**FP139 Cell 92**
Plus 2 minutes grinding			
1	0.29	1.51	0.61
2	0.29	1.02	0.10
3	0.30	1.15	0.26
Mean	0.29	1.23	0.32
s	0.0058	0.25	0.26
RSD (%)	2%	21%	81%
Plus 2 more minutes grinding			
1	0.65	0.99	0.55
2	0.63	1.06	0.73
3	0.52	0.87	0.83
Mean	0.60	0.97	0.70
s	0.070	0.096	0.14
RSD (%)	12%	10%	20%
Remaining sample			
2,4-DNT (µg/g)	0.70	1.05	0.81
Mass of sample (g)	642	697	692

To further test our hypothesis that the 2,4-DNT in the firing point soils is more resistant to the effects of grinding because it is associated with propellant fibers, we added a fiber of M1 propellant (12 mg) to 500 g of Ottawa sand and ground the sand for 60 s, manually obtained twelve 10-g subsamples, and ground the remainder of the sand for an additional four minutes. Likewise, we added four crystals (totaling less than 1 mg) of 2,4-DNT (Standard Analytical Reference Material [SARM]) to another 500 g of Ottawa sand and processed the sand in the same way. The one-minute grind resulted in relative standard deviations

of 53% and 1.7% for the propellant fiber and the SARM samples, respectively (Table 12), thereby supporting our hypothesis. The five-minute grind time reduced the subsampling variance for the propellant fiber sample to 6.5% and had an insignificant effect on the variance for the SARM sample. However, the estimate of the mean of 2,4-DNT was reduced significantly by extended grinding of the SARM-spiked soil, but not in the propellant fiber soil. 2,4-DNT has a relatively high vapor pressure, and the loss from the SARM soil may have been due to heat generation and thermal desorption. Even though the 2,4-DNT that is within a nitrocellulose matrix may be less susceptible to loss by vaporization if the sample is heated, we have adopted the practice of grinding firing point soils for five 60-s intervals with sufficient time between grind cycles to prevent the sample from warming.

Table 11. Extended grinding of three divisions of a multi-increment sample from the 10-m × 10-m grid at FP Mark (FP150). The 12 splits for each were obtained using a rotary divider, and the splits were approximately 60 g each.

	2,4-DNT concentration (µg/g)		
Split	**1 minute**	**3 minutes**	**5 minutes**
1	0.56	0.48	1.17
2	0.52	0.97	1.03
3	1.52	0.87	1.12
4	0.39	0.50	1.35
5	0.62	0.71	1.05
6	0.99	0.42	1.04
7	0.50	0.46	1.04
8	0.61	0.51	1.12
9	1.43	0.71	1.02
10	0.27	0.52	0.98
11	0.40	0.60	1.45
12	0.33	0.52	1.19
Mean	0.68	0.61	1.13
s	0.42	0.17	0.14
RSD (%)	61%	29%	13%

Table 12. Effect of grinding time using a ring mill on mean 2,4-DNT concentration (µg/g) and variance in 10-g subsamples from 500-g samples of Ottawa sand spiked with either a fiber of M1 propellant or grains of SARM 2,4-DNT. Each spiked sample was ground on the ring mill for 60 s and twelve 10-g subsamples were taken for analysis. Then the remainder of the sample was further ground for another four minutes and 12 subsamples were taken for analysis.

	2,4-DNT concentration (µg/g)			
	Unburned propellant fiber		SARM 2,4-DNT	
Replicate	1 minute	5 minutes	1 minute	5 minutes
1	2.44	2.36	1.72	1.16
2	1.00	2.25	1.75	1.16
3	3.19	2.12	1.73	1.15
4	3.06	2.57	1.76	1.17
5	1.08	2.29	1.81	1.14
6	3.94	2.04	1.74	1.11
7	0.92	2.32	1.73	1.14
8	1.73	2.39	1.70	1.19
9	1.79	2.16	1.71	1.16
10	1.26	2.11	1.72	1.14
11	0.92	2.34	1.73	1.16
12	3.27	2.24	1.75	1.13
Mean	2.05	2.27	1.74	1.15
s	1.08	0.15	0.029	0.021
RSD	53%	6.5%	1.7%	1.9%

Size fractionation study

We performed a series of studies to understand which soil size fraction was associated with the 2,4-DNT before and after grinding of firing point soils.

Three 30-increment samples from the 10-m × 10-m grid at FP Mark (FP142, 144, and 149) were divided into three size fractions by passing each sample through #10 (2-mm mesh) and #30 (0.595-mm mesh) sieves. Then each size fraction was extracted with acetone and 2,4-DNT determined. 2,4-DNT was not found in the greater-than-2-mm fraction. For the remaining two fractions, the larger mass of soil was in the less-than-0.595-mm fraction, but the largest mass of 2,4-DNT was in the greater-than-0.595-mm intermediate fraction (Table 13).

We also had a surface soil sample from the propellant burn area at Fort Richardson, Alaska. This sample was collected under the exhaust tube of the burn pan and the sample contained vegetation, unlike the FP Mark soils from the

10-m × 10-m grid. We fractionated this soil into seven size fractions (Table 14) by passing it through a series of sieves: (#10 [2 mm], #18 [1 mm], #30 [0.595 mm], #80 [0.177 mm], #120 [0.125 mm], and #200 [0.075 mm]). The bulk (92%) of the 2,4-DNT was greater than 0.595 mm. Unlike the FP Mark samples, some (7%) of the 2,4-DNT was in the greater-than-2-mm fraction. This difference may be due to the mode of contamination (burning versus firing of howitzers) or the difference in the matrix of the sample (unvegetated versus vegetated).

Table 13. 2,4-DNT in three size fractions of unground 30-increment samples from 10-m × 10-m grid at FP Mark (FP142, FP144 FP149).

Size fraction	Soil mass (kg)	2,4-DNT mass (mg)	2,4-DNT (µg/g)
FP142			
>2 mm	1.87	not detected	not detected
>0.595 mm and <2 mm	0.80	1.51	1.9
<0.595 mm	1.61	0.68	0.42
FP144			
>2 mm	1.26	not detected	not detected
>0.595 mm and <2 mm	0.50	1.65	3.3
<0.595 mm	1.16	0.60	0.51
FP149			
>2 mm	1.6	not detected	not detected
>0.595 mm and <2 mm	0.61	0.78	1.3
<0.595 mm	1.47	0.50	0.34

Table 14. 2,4-DNT in size fractions of a surface sample collected under exhaust tube from Fort Richardson propellant burn pan. Surface was partially vegetated.

Size fraction*	Mass of fraction (g)	Mass of 2,4-DNT (µg)	2,4-DNT (µg/g)
>2 mm	5.9	1,355	229
>1 mm to <2 mm	3.3	13,437	4,069
>0.595 mm to <1 mm	3.4	2,474	723
>0.177 mm to <0.595 mm	11.0	972	88
>0.125 mm to <0.177	2.8	150	54
>0.075mm to <0.125 mm	3.2	153	48
<0.075 mm	5.9	204	35
Mass sum	35.5	18,747	

* Sieves: #10 (2 mm), #18 (1 mm), #30 (0.595 mm), #80 (0.177 mm), #120 (0.125 mm), and #200 (0.075 mm)

Table 15. Size fractionation of five machine-ground splits of a 30-increment sample (FP145) from the 10-m × 10-m grid at FP Mark. Grind time was 1 to 5 minutes. 2,4-DNT was determined in the remaining seven splits without grinding or subsampling.

Soil and 2,4-DNT masses in size fractions.			
	Size fraction mass (g)	**2,4-DNT mass (µg)**	**2,4 DNT soil concentration (µg/g)**
Split 1: 1-minute grind			
>1 mm to <2 mm	0		
>0.595 mm to <1 mm	0		
>0.177 mm to <0.595 mm	10.7	191	18.0
>0.125 mm to <0.177 mm	18.4	10	0.554
>0.075 mm to <0.125 mm	35.8	8.9	0.249
<0.075 mm	134	21	0.154
Total	199	231	1.16 (mean for split)
Split 5: 2-minute grind			
>1 mm to <2 mm	0		
>0.595 mm to <1 mm	0.020		
>0.177 mm to <0.595 mm	2.14	311	145
>0.125 mm to <0.177 mm	2.18	64	29.5
>0.075 mm to <0.125 mm	17.0	56	3.33
<0.075 mm	193	178	0.923
Total	214	610	2.85 (mean for split)
Split 6: 3-minute grind			
>1 mm to <2 mm	0		
>0.595 mm to <1 mm	0.020		
>0.177 mm to <0.595 mm	0.220	56.3	256
>0.125 mm to <0.177 mm	0.440	69.0	157
>0.075mm to <0.125 mm	5.75	49.3	8.57
<0.075 mm	205	134	0.651
Total	212	308	1.46 (mean for split)
Split 8: 4-minute grind			
>1 mm to <2 mm	0		
>0.595 mm to <1 mm	0.230	0.1	0.543
>0.177 mm to <0.595 mm	0.570	7.4	12.9
>0.125 mm to <0.177 mm	0.180	20	111
>0.075 mm to <0.125 mm	1.19	18	15.1
<0.075 mm	202	60	0.299
Total	204	106	0.52 (mean for split)

Table 15 (cont'd).			
Soil and 2,4-DNT masses in size fractions.			
	Size fraction mass (g)	**2,4-DNT mass (µg)**	**2,4 DNT soil concentration (µg/g)**
Split 9: 5-minute grind			
>1 mm to <2 mm	0		
>0.595 mm to <1 mm	0		
>0.177 mm to <0.595 mm	0.600	3.9	6.48
>0.125 mm to <0.177 mm	0.070	9.8	140
>0.075 mm to <0.125 mm	0.810	23	28.1
<0.075 mm	200	68	0.342
Total	201	105	0.52 (mean for split)
Whole sample extractions			
Split 2	203	276	1.36
Split 3	209	199	0.95
Split 4	193	102	0.53
Split 7	198	234	1.18
Split 10	201	59.6	0.30
Split 11	204	144	0.71
Split 12	198	61.2	0.31

To determine the effect of machine grinding on the distribution of 2,4-DNT between the size fractions, we divided one of the 30-increment samples from the 10-m × 10-m grid of FP Mark (FP145) into 12 splits, randomly chose five splits, and ground each for one, two, three, four, or five minutes in the ring mill. Each ground split was fractionated by size into seven size fractions, and the unground splits were extracted whole without subsampling. We found that the ring mill grinder performed according to specifications (i.e., 95% of sample ground to less than 0.075 mm in three minutes) (Table 15); however, after three minutes of grinding, over half of the 2,4-DNT mass was greater than 0.075 mm. After five minutes of grinding, 99.9% of the sample mass was less than 0.125 mm, whereas 87% of the 2,4-DNT mass was less than 0.125 mm (Table 16). These results demonstrate why one minute of grinding was inadequate and why five minutes of grinding reduces the subsampling variance, but not to the extent achievable for crystalline contaminants.

Table 16. Percent of total soil and 2,4-DNT mass that is less than 0.125 mm as a function of grinding time.

Grind time (minutes)	Soil mass <0.125 mm (% of total)	2,4-DNT mass <0.125 mm (% of total)
1	85.3	13
2	98.1	38
3	99.4	60
4	99.6	74
5	99.9	87

Table 17. 2,4-DNT in manually collected subsamples of multi-increment samples from the propellant burn area at OP7 and in samples collected under one corner of the burn pan from which rainwater was dripping. Each sample was ground on a ring mill for 60 seconds prior to subsampling.

Lab ID		2,4-DNT concentration (µg/g)			NG concentration (µg/g)		
		Subsample 1	Subsample 2	Rest of sample	Subsample 1	Subsample 2	Rest of sample
FP170	Surface	7.49	2.15	10.2	4.10	1.54	5.2
FP171	Surface	1.59	2.07	10.0	0.45	0.40	2.4
FP172	Surface	8.05	1.42	10.1	2.20	0.79	2.2
FP173	Surface	4.71	8.27	7.86	3.29	1.24	2.4
FP174	Surface	1.58	6.60	5.39	0.37	1.13	1.9
FP175	Surface	0.99	36.4	5.65	2.09	1.98	2.5
FP176	0–5 cm	28.6	24.4		1.67	1.52	
FP177	5–10 cm	14.4	14.1		not detected	not detected	
FP178	10–15 cm	3.21	2.96		not detected	not detected	

Further evidence that the form of the 2,4-DNT in the surface soils at firing points and burn areas affects our ability to obtain reproducible subsamples is found in the results of our duplicate analyses of subsurface soils obtained under the burn pan of DTA OP7. Rainfall was significant before and during our sample collection activities, and rainwater was dripping from the burn pan onto the ground. We collected a liter of this water and determined 1 mg/L 2,4-DNT by field GC and later confirmed by HPLC-UV. We would expect that any 2,4-DNT detected in the subsurface (greater-than-5-cm depth) would be transported following dissolution in the rainwater, no longer associated with propellant fibers, resulting in reduced subsampling error. Although we have only a few samples, the results of the duplicate analyses of the subsurface soils (Table 17) (Samples

FP177 and 178) are in excellent agreement compared with the results for the 10-g subsamples of surface soils (FP170 to 175) that were ground for 60 s.

Size reduction of vegetated samples using a Retsch cutting mill

The results from the replicate field samples from vegetated firing points demonstrate the difficulty in obtaining samples that can be used to estimate the mean 2,4-DNT concentration in such a complex matrix. Subsampling vegetated field samples is no less challenging; the samples are a mixture of tangled fibers and organic soil (Fig. 15). We used a Type SM1 Retsch Impeller-Type Cutting Mill to reduce some of the field samples from FP Sally (FP186, FP188, FP 222) and FP BoWhale (FP 212, FP 213, and FP 219) to fine powder and measured the subsampling variance associated with manual subsampling and rotary division. Splits from two of the FP Sally samples were fractionated by size as follows.

Two of the ground samples from FP Sally (FP186, FP188) were manually subsampled (5-g subsamples), then the remainder of each sample was split on the rotary divider into twelve subsamples. One split (split #12) from each was fractionated by size and each fraction extracted without subsampling. The remaining splits were extracted whole with acetone. The remaining ground sample from FP Sally (FP222) was split on a rotary divider into 12 bins and each split extracted whole with acetone and 2,4-DNT determined.

The first sample from FP Sally (FP186) was milled using a 0.5-mm mesh on the cutting mill. Subsampling error for manually obtained 5-g subsamples was high (44% RSD), but the error for the rotary-divided subsamples, which were approximately 140 g, was similar to the unvegetated soils ground for five minutes on a ring mill (13% RSD) (Table 18). Size fractionation indicated that the bulk (87%) of the 2,4-DNT mass was in the 0.177-mm to 0.595-mm fraction, while the bulk (88%) of the sample mass was less than 0.177 mm.

The second sample from FP Sally (FP188) was milled using a 0.25-mm mesh, and although this sample had a much lower concentration than the first (0.15 versus 1.08 µg/g), we can see that more of the 2,4-DNT has shifted to the size fractions between 0.075 mm and 0.177 mm in the split that was sieved (Table 19). A third sample from FP Sally (FP222) was ground on the cutting mill and divided using the rotary divider. This sample had a concentration intermediate between the first two FP Sally samples (0.44 µg/g), and the subsampling error was 25% RSD (Table 20).

Two more vegetated samples, both from FP BoWhale (FP212 and FP213), were milled using a 0.25-mm mesh and split using the rotary divider. Two splits from each were further divided by either rotary division or manual fractional

shoveling to determine whether smaller analytical samples could be used to estimate the mean without a substantial increase in variance. The splits for each of the samples were over 100 g, the means estimated from the splits were similar for the two field samples (1.87 and 2.22 µg/g), and the standard deviations were similar (0.36 and 0.38 µg/g), yielding relative standard deviations of 19% and 17% (Tables 21 and 22). Decreasing the analytical sample size to approximately 10 g increased the relative standard deviation to 29% and 35% for the subsamples obtained by rotary division and around 50% for the subsamples obtained by manual fractional shoveling.

Acetone slurry

As an alternative to grinding, Defence Research and Development Canada (DRDC) (Thiboutot et al. 1998) developed a protocol where a soil sample is mixed with acetone to form a slurry. Acetone is an excellent solvent for nitroaromatic, nitramine, and nitrate ester explosives and propellant constituents. The acetone dissolves HE or propellant particulate residues, which are then dispersed through the sample by stirring. The acetone is evaporated, the soil sieved through a #25 mesh (0.71-mm) sieve, and 4-g subsamples obtained manually from the less-than-0.71-mm fraction.

We split one of the 30-increment samples from the 10-m × 10-m grid at FP Mark (FP147) on a rotary divider, and every other split was combined to form two large divisions. One of the divisions was extracted with acetone and 2,4-DNT determined. For the other division, we followed the DRDC protocol. In addition to triplicate 4-g subsamples, we also obtained 12 10-g subsamples to estimate the subsampling variance associated with this procedure. We also extracted and analyzed all the remaining soil that was less than 0.71 mm and the soil fraction that was greater than 0.71 mm and less than 2 mm (Table 23).

The mean 2,4-DNT concentration for the 12 10-g subsamples was 0.74 µg/g, and the relative standard deviation was 2.4%. This low relative standard deviation indicates that the acetone slurry dissolves the 2,4-DNT from the propellant fibers and minimizes the subsampling error associated with particulate residues. The concentration of 2,4-DNT in the division that was extracted without subsampling was 0.93 µg/g, well within the splitting error that we have observed for other samples.

The excellent improvement in subsampling precision observed using the DRDC protocol for firing point soils shows that this procedure has the potential to facilitate both field and laboratory subsampling. Further experiments using the soil fraction that is less than 2 mm (and not using the #25-mesh sieve) should be conducted with firing point and other training range soils.

a. Before milling.

b. After milling.

Figure 15. Composite sample from FP BoWhale before (a) and after (b) passage through Retsch cutting mill.

Table 18. Subsampling error for a vegetated multi-increment surface sample from FP Sally (FP186) processed through a Retsch cutting mill with a 0.5-mm mesh. Split 12 from the rotary divider was fractionated by size and 2,4-DNT was determined in each fraction.

Split #	Mass (g)	2,4-DNT mass (µg)	2,4 DNT soil concentration (µg/g)
Hand-sampled			
1	5	6.09	1.22
2	5	2.69	0.54
3	5	7.60	1.52
4	5	3.86	0.77
		Mean (n = 4)	1.01
		s	0.44
		RSD	44%
Rotary division			
1	142	155	1.09
2	143	142	1.00
3	147	174	1.18
4	149	155	1.04
5	147	127	0.87
6	139	148	1.06
7	144	141	0.98
8	142	136	0.96
9	143	141	0.99
10	139	165	1.19
11	143	167	1.17
12*	132	183	1.39
		Mean (n = 12)	1.08
		s	0.14
		RSD	13%
Sum of masses	1730	1854	
			1.07 µg/g for entire sample

*FP186 rotary division split 12	Mass of fraction (g)	Mass of 2,4-DNT (µg)	2,4-DNT (µg/g)
>2 mm	0		
>1 mm to <2 mm	0.003	not detected	
>0.595 mm to <1 mm	0.004	not detected	
>0.177 mm to <0.595 mm	16.065	158.5	9.87
>0.125 mm to <0.177 mm	11.254	10.9	0.97
>0.075 mm to <0.125 mm	20.518	5.75	0.28
<0.075 mm	83.625	7.96	0.10
Mass sum	132	183	
	1.39 (µg/g) for division		

Table 19. Subsampling error for a vegetated multi-increment surface sample from FP Sally (FP188) ground on a Retsch cutting mill with a 0.25-mm mesh. Split 12 from the rotary divider was fractionated by size and 2,4-DNT was determined in each fraction.

Split #	Mass (g)	2,4-DNT mass (µg)	2,4 DNT soil concentration (µg/g)
Hand-sampled			
1	5	0.26	0.05
2	5	0.94	0.19
3	5	0.23	0.05
4	5	1.05	0.21
		Mean (n = 4)	0.13
		s	0.087
		RSD	67%
Rotary division			
1	143	21.57	0.15
2	148	32.45	0.22
3	149	24.68	0.17
4	143	22.54	0.16
5	152	25.26	0.17
6	141	18.85	0.13
7	152	9.91	0.07
8	132	8.74	0.07
9	116	22.93	0.20
10	149	19.82	0.13
11	144	21.77	0.15
12*	142	16.81	0.12
		Mean (n = 12)	0.15
		s	0.045
		RSD	30%
Sum	1731	248	
		0.14 µg/g for entire sample	

*FP188 rotary division 12	Mass of fraction (g)	Mass of 2,4-DNT (µg)	2,4-DNT (µg/g)
>2 mm	0		
>1 mm to <2 mm	0.003	not detected	not detected
>0.595 mm to <1 mm	0.039	not detected	not detected
>0.177 mm to <0.595 mm	2.100	5.72	2.72
>0.125 mm to <0.177 mm	7.621	7.38	0.976
>0.075 mm to <0.125 mm	21.532	3.70	0.17
<0.075 mm	110.332	not detected	not detected
Mass sum	142	16.8	
	0.12 µg/g for division		

Table 20. Rotary division of vegetated multi-increment surface sample from FP Sally ground (FP222) on a Retsch cutting mill.

Split #	Mass (g)	2,4-DNT mass (µg)	2,4 DNT soil concentration (µg/g)
1	183	82.0	0.45
2	185	110	0.59
3	183	73.8	0.40
4	175	66.9	0.38
5	173	63.5	0.37
6	178	83.8	0.47
7	162	50.0	0.31
8	179	72.0	0.40
9	185	105	0.57
10	180	75.1	0.42
11	170	53.7	0.32
12	195	126	0.65
Sum	2148	962	
		Mean	0.44
		s	0.11
		RSD	25%

Table 21. Division of vegetated multi-increment surface sample from FP BoWhale (FP212) ground on a Retsch cutting mill.			
Rotary division			
Split #	**Mass (g)**	**2,4-DNT mass (µg)**	**2,4 DNT soil concentration (µg/g)**
1	104	213	2.05
2	114	177	1.55
3	118	193	1.63
4	115	250	2.17
5	122	202	1.65
6	120	270	2.25
7	122	304	2.49
8	111	164	1.47
9	116	212	1.83
10	Split by rotary divider		1.3
11	117	247	2.11
12	Split by fractional shoveling		2.02
			Mean =1.88
			s = 0.36
			RSD = 19%
Split #10 rotary division replicates			
10-7	9.9	10.5	1.1
10-8	8.9	10.6	1.2
10-9	9.0	7.96	0.88
10-10	8.5	14.9	1.8
10-11	7.5	7.00	0.93
10-12	7.4	10.9	1.5
			Mean* = 1.2 s* = 0.35 RSD = 29%
10-1 to 10-6	59	80.3	1.4
Sum of masses for split 10	110	142	Conc. for split #10 = 1.3

Table 21 (cont'd). Division of vegetated multi-increment surface sample from FP BoWhale (FP212) ground on a Retsch cutting mill.

Split #12 fractional shoveling replicates			
12-1	9.42	17.9	1.90
12-2	8.69	22.7	2.61
12-3	10.4	17.6	1.69
12-4	9.54	16.2	1.70
12-5	8.27	38.1	4.61
12-6	8.90	15.8	1.78
12-7	8.89	11.1	1.25
12-8	8.17	23.8	2.91
12-9	8.38	8.66	1.04
12-10	9.01	14.6	1.62
12-1	8.79	13.5	1.54
12-12	8.62	13.5	1.57
Sum of masses for split 12	107	214	Mean = 2.02 s = 0.97 RSD = 48%

* Mean and standard deviation for splits 10-7 to 10-12. Splits 10-1 to 10-6 were combined and extracted as one sample.

Table 22. Division of vegetated multi-increment surface sample from FP BoWhale (FP213) ground on a Retsch cutting mill.			
Split #	**Mass (g)**	**2,4-DNT mass (µg)**	**2,4 DNT soil concentration (µg/g)**
Rotary division			
1	123	265	2.15
2	116	226	1.95
3	115	245	2.13
4	**Split by fractional shoveling**		1.89
5	**Split by rotary divider**		2.6
6	107	212	1.98
7	117	212	1.81
8	113	240	2.12
9	122	248	2.03
10	115	260	2.26
11	117	362	3.09
12	120	320	2.67
			Mean = 2.22 s = 0.38 RSD = 17%
Split #5 rotary division replicates			
5-1	9.5	15.1	1.6
5-2	9.5	26.2	2.8
5-3	11	32.8	3.0
5-4	9.8	10.0	1.0
5-5	10	27.2	2.7
5-6	10	21.2	2.1
			Mean* = 2.2 s* = 0.78 RSD = 35%
5-7 to 5-12	60	179	3.0
Sum of masses for split 5	120	311	Conc. for split #5 = 2.6

Table 22 (cont'd). Division of vegetated multi-increment surface sample from FP BoWhale (FP213) ground on a Retsch cutting mill.

Split #4 fractional shoveling replicates			
4-1	9.87	12.8	1.30
4-2	9.44	15.5	1.64
4-3	9.79	43.1	4.40
4-4	10.23	28.0	2.74
4-5	9.50	11.5	1.21
4-6	9.66	21.6	2.24
4-7	9.90	22.1	2.23
4-8	9.33	19.5	2.09
4-9	9.26	10.8	1.17
4-10	9.87	14.6	1.48
4-11	9.26	11.0	1.19
4-12	9.82	9.32	0.948
Sum of masses for Split 4	116	220	Mean = 1.89 s = 0.96 RSD = 53%

* Mean and standard deviation for splits 5-1 to 5-6. Splits 5-7 to 5-12 were combined and extracted as one sample.

Table 23. 2,4-DNT concentrations found in subsamples of a 30-increment sample (FP147) collected from the 10-m × 10-m grid at FP Mark. Half of the sample (Division A) was saturated with acetone, stirred, the acetone evaporated, and the soil passed through a 25-mesh (0.71-mm) sieve prior to subsampling (according to the soil processing protocol developed at DRDC [Thiboutot et al. 1998]). 2,4-DNT was determined in the other half (Division B) of the sample without subsampling. For the entire sample, 1,497 µg of 2,4-DNT was determined in 1,920 g of soil, yielding a concentration of 0.78 µg/g.

FP147 Division A: Acetone slurry	2,4-DNT (µg/g)
4-g subsamples	0.77
	0.80
	0.82
Mean	0.80
10-g subsamples	
	0.79
	0.73
	0.73
	0.74
	0.74
	0.75
	0.72
	0.74
	0.74
	0.73
	0.75
	0.73
Mean	0.74
s	0.018
RSD	2.4 %
Remaining sample from acetone slurry (537 g)	0.70
Fraction <2 mm and >0.71 mm from acetone slurry (260 g)	0.41
FP147 Division B: Extracted without subsampling (991 g)	0.93

4 DISCUSSION

Field sample collection

The 95% upper confidence limit of the mean concentration of 2,4-DNT in a 10-m × 10-m grid on a sparsely vegetated firing point was estimated using replicate multi-increment samples. The limit based on 10 30-increment samples was nearly identical to that obtained from 20 10-increment samples from randomly selected 1-m^2 cells within the 100-m^2 grid. In contrast, a statistically valid upper confidence limit could not be determined based on 100 discrete samples because the data were not normally distributed. An individual discrete sample from a 1-m × 1-m cell of a 10-m × 10-m grid was inadequate to represent the 2,4-DNT residue within the cell, much less the larger grid. The individual discrete samples lacked sufficient mass to adequately represent the composition of the surface soil. These results for discrete samples are similar to those obtained using a similar sampling scheme on an artillery/mortar impact area at Fort Polk (Jenkins et al. 2004). Duplicate discrete samples differed by up to three orders of magnitude in RDX concentrations. However, estimates of the average RDX concentration using replicate multi-increment samples from the 100-m^2 grid on the impact area also differed significantly. The authors attribute the lack of agreement between replicate multi-increment samples to the presence of a few localized areas of high RDX concentration and the fact that only some of the multi-increment samples contained increments collected from within the high concentration zones. Also, the energetic materials are crystalline particles within the high concentration zones, and each individual increment taken from within the high concentration zones may not have been of sufficient mass to mitigate the error associated with the compositional heterogeneity. As a result, individual increments from within the high concentration zones may not have had a high analyte concentration because the energetic particles were underrepresented. Research is ongoing to determine whether larger samples masses (to minimize sampling error due to compositional heterogeneity) and/or more increments (to minimize the sampling error due to distributional heterogeneity) can provide repeatable estimates of average concentration of energetics in the surface soil of impact areas.

At DTA, we demonstrated that multi-increment samples could not only represent a 100-m^2 area of a firing point, but also a much larger area of a sparsely vegetated firing point. Multi-increment samples from a wide area (10,800 m^2) that were collected by multiple samplers using a systematic random approach (Fig. 5) provided estimates of the mean 2,4-DNT concentration with a relative

standard deviation of about 25%. Fifty-increment samples provided an estimate of the mean that was not significantly different from that provided by 200-increment samples, and the 95% upper confidence limits were similar. The precision of field replicates was similar for 33- to 40-increment samples collected around a propellant burn pan where the estimated concentration of 2,4-DNT was an order of magnitude higher than that at the sparsely vegetated firing point.

In contrast, 50-increment samples from vegetated firing points did not provide normally distributed estimates of mean concentration. Differences between samplers were evident, perhaps reflecting differences in sampling depth. Further studies with more increments and consistent sampling depth are needed to verify this assumption. In any case, replication of field samples by each field sampler is recommended to determine whether biases are introduced by individual sampling techniques.

Laboratory processing and subsampling

We performed a series of experiments to evaluate the compositional and distributional heterogeneity associated with propellant residues. Starting with the hypothesis that 2,4-DNT is coupled with propellant fibers, proper laboratory subsampling of firing point soils requires that each subsample has adequate mass to contain the same proportion of fibers as the field sample. For example, if the field sample contains one fiber in each 20 grams of soil, collection of only two grams of soil for extraction will not represent the proportion of fibers in the field sample. In this case most of the samples will show a very low concentration of 2,4-DNT and some of the subsamples will show a higher concentration of 2,4-DNT than actually exists in the field sample. Also, the subsample must be formed by taking an adequate number of increments to overcome any segregation of the fibers within the field sample. The best method available is a rotary divider that forms subsamples with hundreds of random increments. When we used a rotary divider to split an 11-kg sample into 12 900-g subsamples (Table 7), the range of 2,4-DNT concentrations was 0.50 to 1.28 µg/g, the mean was 0.76, and the relative standard deviation was 28%. The fact that 900-g soil subsamples failed to effectively represent fibers in the 11-kg field sample indicates that subsample masses that are typically taken for analysis (tens of grams at most) cannot represent the field sample with any degree of confidence. Either the entire field sample needs to be extracted for analysis or some form of laboratory processing is needed to improve the precision and accuracy of subsampling.

We focused most of our laboratory processing on comminution to diminish the fiber particle sizes and increase the number of fiber particle fragments in our field samples, which should reduce the subsample mass required to represent the

field sample. We found that the protocol that we developed for soils contaminated with high explosives (e.g., grinding for 60 s using a ring mill) did not reduce the subsampling variability for propellant-contaminated soils. Grinding for a longer period of time, up to five minutes, did reduce the subsampling variability for field-contaminated soils and a soil spiked with a piece of propellant, but not always to the extent of that obtained after 2,4-DNT was added as crystalline material to clean sand and the sample ground.

We performed sieve analyses to fractionate field-contaminated samples and found that the size fraction between 0.595 mm and 2 mm contained most of the 2,4-DNT mass. Sieve analysis of ground field-contaminated soils showed that 85% of the soil mass was less than 0.125 mm after grinding for one minute, but five minutes of grinding was needed to reduce 87% of the DNT mass to the less-than-0.125-mm size fraction. The propellant fibers are much more difficult to comminute than the soil particles, thus requiring longer grind times.

Two issues concerning grinding time need to be addressed. First, a low relative standard deviation does not necessarily indicate that all the propellant fibers are pulverized sufficiently. In one of our experiments, three minutes of grinding resulted in a relative standard deviation of the mean of only 2% for triplicate subsamples (Table 10), but the estimate of the mean doubled after an additional two minutes of grinding of the same sample, indicating that some fibers were not pulverized. Secondly, heat generation due to friction between the puck, soil, and bowl is undesirable for analytes that may thermally desorb or degrade. Our current practice for propellant-contaminated soils is to grind for five 60-s cycles with at least 60-s rest between grinding cycles.

In addition to grinding soil samples, we used a cutting mill to process samples composed of the organic surface of vegetated firing points. We suspect that the fibrous nature of these samples is similar to the fibrous nature of propellant grains (e.g., a matrix composed primarily of cellulose). In all cases, the subsampling variance for rotary-divided milled samples was less than for manual subsampling. Improved precision with an increased number of increments implies that distributional heterogeneity was the major contributor to subsampling variance for these samples.

There are two alternatives to grinding or milling samples, both of which use acetone to dissolve 2,4-DNT from the propellant matrix. One alternative is to extract the entire sample with acetone. This procedure worked well for soils with propellant residues and has been used successfully for soils containing particles of high explosives (Radtke et al. 2003). The second procedure, which is appropriate for soils but not for fibrous organic samples (unless they have been milled), is to add sufficient acetone to the undivided field sample to form a slurry. Acetone

will dissolve 2,4-DNT, and once the acetone is evaporated, the 2,4-DNT should be more evenly distributed throughout the sample than when it is associated with the propellant fibers. The subsampling precision we obtained using this slurry approach for one soil sample was excellent (2.4%). Issues that remain to be studied are the appropriate procedures for sieving to remove the oversize fraction and whether vaporization of the more volatile analytes, such as NG, may be enhanced. The major disadvantage of both of these alternatives is the use of relatively large volumes of solvent. Although acetone has low toxicity, the Code of Federal Regulations (40CFR261.33) lists acetone as a hazardous waste if and when it is intended to be discarded. The listing is due to acetone's ignitability. Capturing of volatile emissions and disposing or recycling of used acetone need to be planned.

5 RECOMMENDATIONS

One of our objectives was to develop sampling methods to determine mean concentrations of 2,4-DNT in the surface soil (top 2.5 cm) of a sparsely vegetated 105-mm firing point with statistical confidence that the mean is above or below the soil cleanup level. The Alaska Department of Environmental Conservation soil cleanup levels for 2,4-DNT are 0.005 µg/g for migration to groundwater and 12 µg/g for ingestion, which is also the maximum "alternate cleanup level" that is based on site-specific conditions. Given that FP Mark is on an Army training range, the 12 µg/g cleanup level is more realistic for our purposes. Multi-increment samples composed of 50 increments collected at regular intervals across the entire sampling unit (10,800 m^2) provided estimates of mean 2,4-DNT concentrations that were normally distributed, and therefore an upper confidence limit for the mean could be computed. We found that for FP Mark, the estimated upper confidence limit for the mean concentration of 2,4-DNT was less than 1 µg/g, well below a cleanup level of 12 µg/g.

Sampling methods for vegetated firing points need to be refined. More increments and more control of sampling depth are two improvements that need to be explored.

Our second objective was to reduce the laboratory subsampling error associated with soils from firing points. Through size fractionation studies, we found that most of the analyte of interest, 2,4-DNT, was found in the 0.595- to 2-mm size range, although the bulk of the soil was less than 0.595 mm. Machine grinding using a ring mill for five minutes was required to move 87% of the 2,4-DNT to the size fraction containing 99.9% of the soil (<0.125 mm). These results support the hypothesis that the 2,4-DNT remains in a nitrocellulose matrix when it is deposited at a firing point. Isolation and characterization of propellant residue fibers would allow us to apply sampling theory (Pitard 1993) to confirm appropriate sampling procedures.

6 CONCLUSIONS

Based on field and laboratory subsampling experiments, 2,4-DNT in soils from firing points is in a particulate form that resists comminution. Evidence suggests that the 2,4-DNT remains in the nitrocellulose matrix of single-base propellants as discrete fibers distributed on the soil surface. Estimation of mean concentrations of 2,4-DNT at firing points requires that field samples contain an adequate number of increments and adequate mass to represent the distribution and composition of propellant fibers in the surface soil.

Collection of replicate 50-increment samples, where the <2-mm fraction was approximately 3 kg, was found to be adequate to estimate a statistically valid upper confidence limit of the mean concentration of 2,4-DNT from a 10,800-m^2 area of a sparsely vegetated firing point. Accurate estimation of 2,4-DNT in the multi-increment samples required that the entire sample be extracted with solvent. Alternatively, the entire sample had to be processed either by sequential grinding on a ring mill for five minutes or solvent used to dissolve the 2,4-DNT from the nitrocellulose fiber and disperse it throughout the bulk sample.

The mean concentrations of 2,4-DNT at the DTA firing points are in the low parts per million range (µg/g). Concentrations are about one order of magnitude higher at propellant burn-pan locations. Annual collection of multi-increment samples can be used to monitor the accumulation and persistence of 2,4-DNT at firing points and burn areas.

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APPENDIX A. 2,4-DNT CONCENTRATIONS (µg/g) DETERMINED IN A 10-m × 10-m GRID AT FP MARK.

2,4-DNT was determined in the fraction that was less than 2 mm.

Table A1. Ten-increment samples from 1-m × 1-m cells in 10-m × 10-m grid at FP Mark.

Lab ID	Cell ID	Total sample mass (kg)	Mass of soil <2-mm (kg)	Mass of 2,4-DNT (mg)	2,4-DNT concentration (µg/g)
FP121	7	1.42	0.72	0.78	1.09
FP122	8	1.49	0.63	0.15	0.24
FP123	12	1.10	0.56	0.52	0.92
FP124	19	1.76	0.72	0.34	0.47
FP125	27	1.33	0.74	0.54	0.73
FP126	28	1.43	0.71	1.22	1.72
FP127	34	1.24	0.65	0.71	1.10
FP128	35	1.25	0.70	0.91	1.30
FP129	37	1.43	0.63	0.73	1.16
FP130	39	1.22	0.78	1.07	1.37
FP131	46	1.62	0.90	1.15	1.27
FP132	52	1.34	0.71	0.55	0.78
FP133	58	1.70	0.80	0.82	1.03
FP134	66	1.48	0.74	0.70	0.95
FP135	70	1.78	1.07	1.03	0.96
FP136	74	1.35	0.70	0.56	0.79
FP137	77	1.37	0.85	0.64	0.76
FP138	80	1.40	1.02	0.34	0.33
FP139	92	1.55	0.79	0.63	0.80
FP140	96	1.72	0.80	0.77	0.96
Sum		28.98	15.22	14.16	
Mean					0.94
Median					0.96
Minimum					0.24
Maximum					1.72
s					0.353

Table A2. Thirty-increment samples from 10-m × 10-m grid at FP Mark.				
Lab ID	Total sample mass (kg)	Mass of soil <2-mm (kg)	Mass of 2,4-DNT (mg)	2,4-DNT concentration (µg/g)
FP141	3.99	2.26	1.36	0.60
FP142	4.31	2.41	2.19	0.91
FP143	3.78	1.95	1.72	0.88
FP144	2.93	1.66	2.25	1.36
FP145	4.42	2.44	2.44	1.00
FP146	3.74	2.03	2.54	1.25
FP147	3.41	1.92	1.5	0.78
FP148	4.11	2.22	2.40	1.08
FP149	3.67	2.08	1.28	0.62
FP150	4.23	2.31	1.86	0.81
sum	38.59	21.28	19.54	
Mean				0.93
Median				0.90
Minimum				0.60
Maximum				1.35
s				0.249

Table A3. Discrete samples from 10-m × 10-m grid at FP Mark.				
Lab ID	Cell ID	Total sample mass (g)	Mass of soil <2-mm (g)	2,4-DNT concentration (µg/g)
FP001	1	98.00	63.06	2.71
FP002	2	91.25	50.96	0.65
FP003	3	96.94	56.13	0.56
FP004	4	75.60	47.73	1.60
FP005	5	111.63	59.44	1.26
FP006	6	89.23	47.15	1.25
FP007	7	92.50	48.51	2.63
FP008	8	108.37	50.87	0.64
FP009	9	107.50	56.56	0.18
FP010	10	92.12	45.26	0.19
FP011	11	100.71	48.13	0.40
FP012	12	93.75	60.77	0.67
FP013	13	104.16	62.81	0.20
FP014	14	116.57	57.32	1.71
FP015	15	111.07	51.15	6.38
FP016	16	80.91	59.49	2.00
FP017	17	118.74	49.39	0.41
FP018	18	110.95	52.46	0.34
FP019	19	130.49	57.15	0.18
FP020	20	106.97	49.76	1.15
FP021	21	100.77	49.69	1.52
FP022	22	99.75	54.5	1.96
FP023	23	118.47	61.77	1.07
FP024	24	99.60	54.83	0.51
FP025	25	94.33	54.96	4.18
FP026	26	126.75	45.96	0.06
FP027	27	101.56	55.78	1.13
FP028	28	83.58	38.66	0.02
FP029	29	124.17	58.8	0.35
FP030	30	100.77	53.14	1.83
FP031	31	100.38	57.09	1.68
FP032	32	114.21	60.97	0.18

Table A3 (cont'd).				
Lab ID	Cell ID	Total sample mass (g)	Mass of soil <2-mm (g)	2,4-DNT concentration (µg/g)
FP033	33	101.49	62.71	1.00
FP034	34	106.17	57.02	1.05
FP035	35	110.93	66.62	2.68
FP036	36	120.53	49.54	1.74
FP037	37	114.21	50.58	0.37
FP038	38	112.33	45.82	0.29
FP039	39	79.08	53.26	3.45
FP040	40	114.40	54.15	1.51
FP041	41	95.45	54.42	0.96
FP042	42	99.24	56.53	1.06
FP043	43	97.03	63.88	3.08
FP044	44	97.84	44.92	1.64
FP045	45	103.27	67.69	0.27
FP046	46	89.02	54.26	1.95
FP047	47	104.54	49.58	0.36
FP048	48	117.43	58.2	0.06
FP049	49	112.59	58.59	0.93
FP050	50	100.64	56.22	0.67
FP051	51	58.74	52.98	0.59
FP052	52	113.27	64.87	1.22
FP053	53	97.61	64.65	1.13
FP054	54	117.50	66.43	0.87
FP055	55	101.92	52.67	0.66
FP056	56	87.50	53.13	0.26
FP057	57	108.10	63.94	1.62
FP058	58	96.78	56.72	0.15
FP059	59	105.26	50.28	0.61
FP060	60	77.49	66.16	0.008
FP061	61	99.36	69.78	0.71
FP062	62	110.03	74.54	0.68
FP063	63	99.63	56.47	4.78
FP064	64	93.61	65.63	3.38
FP065	65	104.92	57.31	2.39

Table A3 (cont'd). Discrete samples from 10-m × 10-m grid at FP Mark.				
Lab ID	Cell ID	Total sample mass (g)	Mass of soil <2-mm (g)	2,4-DNT concentration (µg/g)
FP066	66	122.53	50.03	0.01
FP067	67	111.26	54.9	0.24
FP068	68	92.79	54.25	0.63
FP069	69	86.21	73.46	0.001
FP070	70	79.46	68.52	0.002
FP071	71	77.24	48.72	1.86
FP072	72	93.93	53.24	3.44
FP073	73	108.93	42.57	0.23
FP074	74	77.56	43.8	1.03
FP075	75	75.42	46.48	0.15
FP076	76	82.02	49.49	0.13
FP077	77	103.61	52.76	0.18
FP078	78	79.94	38.68	1.38
FP079	79	73.14	58.17	0.57
FP080	80	94.51	55.15	1.06
FP081	81	85.81	48.91	0.07
FP082	82	104.24	61.58	1.59
FP083	83	80.09	42.77	0.36
FP084	84	111.26	51.63	0.04
FP085	85	130.79	61.33	0.27
FP086	86	102.59	58.82	0.03
FP087	87	126.68	56.81	0.11
FP088	88	103.93	48.01	0.50
FP089	89	85.46	65.87	0.07
FP090	90	70.94	64.74	0.58
FP091	91	72.53	39.1	0.98
FP092	92	73.68	53.35	2.72
FP093	93	98.35	56.12	0.26
FP094	94	75.48	56.33	3.88
FP095	95	63.13	48.46	1.18
FP096	96	156.56	67.01	0.32
FP097	97	188.36	66.19	0.0007
FP098	98	129.01	59.5	0.44

Table A3 (cont'd).				
Lab ID	Cell ID	Total sample mass (g)	Mass of soil <2-mm (g)	2,4-DNT concentration (µg/g)
FP099	99	156.62	81.78	0.004
FP100	100	136.60	55.21	0.002
FP101	7 Duplicate	97.38	51.03	1.05
FP102	8 Duplicate	139.23	54.09	0.009
FP103	12 Duplicate	105.89	59.01	1.49
FP104	19 Duplicate	136.19	58.64	0.22
FP105	27 Duplicate	102.14	58.31	0.15
FP106	28 Duplicate	132.04	63.08	0.19
FP107	34 Duplicate	93.07	65.77	0.65
FP108	35 Duplicate	122.28	79.84	0.20
FP109	37 Duplicate	133.05	68.85	1.41
FP110	39 Duplicate	100.89	71.9	1.71
FP111	46 Duplicate	90.07	59.53	0.80
FP112	52 Duplicate	100.06	60.78	0.61
FP113	58 Duplicate	115.99	59.98	0.10
FP114	66 Duplicate	143.11	75.18	0.74
FP115	70 Duplicate	100.38	80.00	0.13
FP116	74 Duplicate	111.15	59.76	0.60
FP117	77 Duplicate	109.56	61.22	0.45
FP118	80 Duplicate	89.35	75.52	0.22
FP119	92 Duplicate	89.85	66.19	2.10
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13. SUPPLEMENTARY NOTES

14. ABSTRACT

At firing points for 105-mm howitzers, 2,4-DNT is detectable in the surface soils. 2,4-DNT is listed as a hazardous substance by the EPA and several states, including Alaska. Sample collection methods and laboratory subsampling procedures were developed to estimate the mean concentration of 2,4-DNT at a sparsely vegetated firing point. Collection of replicate 50-increment samples, where the <2-mm fraction was approximately 3 kg, was found to be adequate to estimate a statistically valid upper confidence limit of the mean concentration of 2,4-DNT from a 10,800-m^2 area. The 95% upper confidence limit was 0.7 µg/g for multi-increment samples collected by five different samplers. In contrast, collection of replicate 50-increment samples from heavily vegetated firing points did not provide normally distributed estimates of 2,4-DNT concentrations, indicating that more increments and more mass are needed per sample. Sample corers that yield uniform sampling depths of vegetated surfaces may also improve precision of the field samples. Accurate estimation of 2,4-DNT in the multi-increment samples required that the entire sample be extracted with solvent or the entire sample be subjected to grinding on a ring mill. Size fractionation studies revealed that most of the 2,4-DNT in the firing range soils was in the 0.595- to 2-mm size range, although the bulk of the soil was less than 0.595 mm prior to grinding. The 2,4-DNT appears to be in particulate form, most likely within fibers of the nitrocellulose-based propellant. Grinding for five minutes was needed to pulverize the propellant fibers sufficiently so that analytical subsamples could be obtained in a reproducible manner. We have adopted the practice of grinding firing point soils for five one-minute intervals, with time for heat dissipation between grinds, prior to obtaining replicate 10-g subsamples.

15. SUBJECT TERMS

2,4-DNT
Propellant residue
Soil sampling
Soil subsampling

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